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Anionic Polymerization of *trans*-β-Methylstyrene

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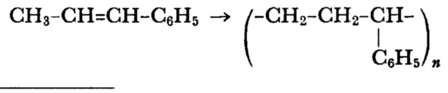
The anionic polymerization of *trans*-β-methylstyrene by *n*-butyllithium was carried out in hydrocarbon solvents and in tetrahydrofuran. In hydrocarbon solvents the monomer was consumed by *n*-butyllithium, but gave no polymer insoluble in methanol. In tetrahydrofuran the polymerization proceeded rapidly, giving a polymer insoluble in methanol. This polymer was produced by the normal addition polymerization of a C=C double bond. The relatively lower degree of polymerization of poly-β-methylstyrene indicated a chain transfer in the reaction. The chain transfer reaction due to the active hydrogen of a methyl group in this monomer was also observed by means of the electronic spectra of the reaction mixtures. The polymer anion was converted to inactive anions at high temperatures.

Staudinger[1] proposed that β-methylstyrene may be polymerized by a cationic initiator to give the so-called 1, 3-polymer by means of a hydrogen shift mechanism:



$$CH_3\text{-}CH{=}CH\text{-}C_6H_5 \rightarrow \left(\text{-}CH_2\text{-}CH_2\text{-}\underset{C_6H_5}{\underset{|}{CH}}\text{-}\right)_n$$

Recently, however, the reexamination of this cationic polymerization has proved that β-methylstyrene polymerizes only by means of the usual mechanism through the opening of a C=C double bond.[2,3]

On the other hand, regarding the anionic

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[1] H. Staudinger and E. Dreher, *Ann.*, **517**, 73 (1935).

[2] J. P. Kennedy, *J. Polymer Sci.*, **A2**, 5171 (1964).

[3] S. Murahashi, S. Nozakura, K. Tsuboshima and Y. Kotake, This Bulletin, **38**, 156 (1965).

polymerization of β-methylstyrene only a little information is available in the literature.4,5) The present authors investigated the anionic polymerization of this monomer using *n*-butyllithium as a catalyst. It was found that in tetrahydrofuran the polymerization of this monomer took place by the normal addition of a C=C double bond, accompanied by the chain transfer to the monomer. The electronic spectra of the reaction mixtures were also investigated in order to correlate them with the reaction mechanism.

Experimental

***trans*-β-Methylstyrene (β-MeSt).** According to the method of Park,6) β-methylstyrene was prepared by the dehydration of ethylphenylcarbinol with alumina at 300±10°C. The *trans*-isomer was collected by fractional distillation and was purified by redistillation under nitrogen from a flask containing lithium aluminum hydride. The purity was checked by gas chromatography. Bp 76—77°C/28 mmHg, n_D^{20} 1.5504: lit.,7) n_D^{20} 1.5507.

Tetrahydrofuran (THF). Tetrahydrofuran which had been dried over sodium was refluxed over lithium aluminum hydride and then transferred by a vacuum system to a glass ampule before use.

Benzene and *n*-Hexane. Each solvent was purified by the usual method8) and before use was transferred by the vacuum line from a flask containing a small amount of *n*-butyllithium to an ampule.

***n*-Butyllithium (*n*-BuLi).** *n*-Butyllithium was prepared in *n*-heptane according to the method of Ziegler.9) The concentration was determined by the double-titration method of Gilman.10)

Sodium Naphthalene (Na-Naph). Sodium naphthalene was prepared in tetrahydrofuran;11) its concentration was determined by titration with 0.1 N hydrochloric acid, using phenolphthalein as an indicator.

Sodium-dispersion (Na-disp.). Sodium-dispersion in *n*-octane was used; the concentration was 30%.

Polymerization. The polymerization was carried out in a glass ampule which had been cleaned and dried completely. The solvent was first transferred into a glass ampule by means of a vacuum line, and then the monomer and initiator were added by syringes under an atomosphere of dried nitrogen. The solution was then allowed to stand in a constant temperature bath. The reaction was terminated by the addition of a trace of methanol. The concentration of unchanged *trans*-β-methylstyrene was determined spectrophotometrically by using a part of the solution. The optical density was measured at 293.5 mμ (ε_{max} 790), where it obeyed Beer's law. On the other hand, the residual solution was poured into a large amount of methanol and the precipitated polymer was separated by filtration, dried, and weighed.

In the following, the monomer consumption obtained by the spectrophotometric measurements and the yield of the methanol-insoluble polymer will be defined as "conversion" and "yield" respectively, while "polymer" will refer to the methanol-insoluble part otherwise stated.

Measurement. The molecular weight of the polymer was determined cryoscopically in a benzene solution. The infrared spectrum was measured on a Nihon Bunko DS-21 Spectrometer. The NMR spectrum was obtained in a carbon tetrachloride solution using a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co., Ltd.) at 100 Mc/sec, by using tetramethylsilane as an internal standard. The electronic spectrum was obtained with a Hitachi Perkin-Elmer 139 Spectrophotometer or a Hitachi EPS-2 Spectrophotometer. The spectrum of the living anion was measured in tetrahydrofuran according to the technique of Waack.12)

Results

Polymerization in Hydrocarbon. Polymerizations were carried out in hydrocarbon solvents using *n*-BuLi, sodium-dispersion, and sodium naphthalene as initiators. The results are summarized in Table 1. A yellow color appeared two or three hours after the addition of an initiator, and its intensity gradually increased. When the reaction was performed for a prolonged time, it was observed that a considerable amount of the monomer was consumed, but no methanol-insoluble polymer was obtained. However, a small amount of the polymer was obtained in the polymerization where sodium naphthalene was used as an initiator and where a trace of tetrahydrofuran was present as the solvent of the initiator solution.

Polymerization in Tetrahydrofuran. The polymerization of *trans*-β-methylstyrene with *n*-BuLi was carried out in tetrahydrofuran. As soon as *n*-BuLi was added to the monomer solution, a red color appeared; the density of this color did not change during the reaction at room temperature.

The time dependencies of the conversion (obtained from the UV spectrum) and the yield (wt% of the methanol-insoluble polymer against the monomer charged) at 0 and 30°C are shown in Fig. 1. The monomer consumption was quantitative after 24 hr, but the yield of the methanolinsoluble polymer was much less than that. The molecular weights of the polymers obtained at 0 and 30°C were

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4) H. F. Herbranderson and D. S. Mooney, *J. Am. Chem. Soc.*, **79**, 5809 (1957).

5) D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *ibid.*, **85**, 553 (1963).

6) W. R. R. Park and G. F. Wright, *J. Org. Chem.*, **19**, 1435 (1954).

7) C. G. Overberger, D. Tanner and E. M. Pearce, *J. Am. Chem. Soc.*, **80**, 4566 (1958).

8) A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd Ed., Interscience Publishers, New York (1955).

9) K. Ziegler and A. Colonius, *Ann.*, **479**, 135 (1930).

10) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

11) M. Morton and R. Milkovich, *J. Polymer Sci.*, **A1**, 443 (1963).

12) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

TABLE 1. POLYMERIZATION OF *trans*-β-METHYLSTYRENE IN HYDROCARBON SOLVENT
Monomer, 10 mmol; solvent, 20 m*l*

Solvent	Initiator	Monomer / Initiator (mol/mol)	Temp. °C	Time day	Conv.[a] %	Yield[b] %
Benzene	*n*-BuLi	30	30	88	14.3	0
Benzene	Na-disp.	44	30	44	—	0
Benzene	*n*-BuLi	90	60	90	9.0	0
Hexane	Na-disp.	2	60	90	51.3	0
None	Na-Naph	90	30	90	—	6.6

a) Obtained from UV spectrum. b) Methanol - insoluble polymer.

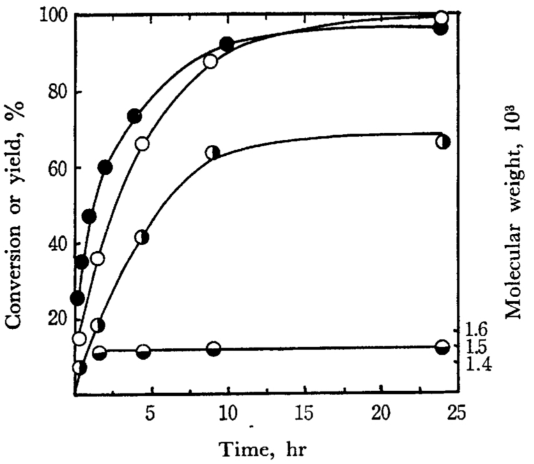


Fig. 1. Anionic polymerization of *trans*-β-methylstyrene by *n*-BuLi in THF.—Time *vs.* conversion.
○: Conversion at 0°C
●: Conversion at 30°C
◑: Yield of methanol insoluble polymer at 0°C
◒: Molecular weight of methanol - insoluble polymer obtained at 0°C, $[M]_0$ 0.41 mol/*l*, [*n*-BuLi] 4.5×10^{-3} mol/*l* at 0°C, 4.0×10^{-3} mol/*l* at 30°C.

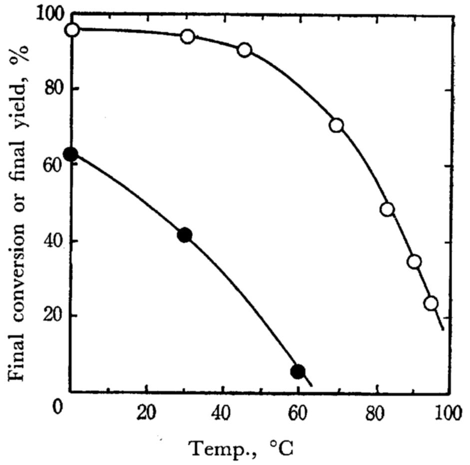


Fig. 2. Anionic polymerization of *trans*-β-methylstyrene by *n*-BuLi in THF.—Effect of temperature.
○: Final conversion
●: Final yield
$[M]_0$ 0.43 mol/*l*
[*n*-BuLi] 0.43—0.49×10^{-2} mol/*l* Time 48 hr

about 1500 and 1300 respectively and were independent of the yield.

It was found that when the reaction ceased the monomer remained unchanged at high reaction temperatures. In order to investigate the effects of the temperature on the final conversion and the final yield, prolonged reactions were carried out at various temperatures between 0 and 100°C, using *n*-BuLi as an initiator. The results are shown in Fig. 2. The curves show that both the final conversion and the final yield gradually decreased at elevated temperatures. The color of the reaction mixture was red at 0 and 30°C, but turned purple above 60°C. A similar tendency was also observed in the polymerization initiated by sodium naphthalene.

The polymerization was carried out for 48 hr at 30°C, while varying the concentration of *n*-BuLi. As shown in Fig. 3, the final conversion, the final yield, and the molecular weight of the polymer were all independent of the concentration of *n*-BuLi.

The relationships between the final yield of the methanol-insoluble polymer and the initial monomer concentration are shown in Fig. 4. The yield increased with an increase in the initial monomer concentration independently of the reaction temperature. However, the yield at 30°C was less than that at 0°C with each initial monomer concentration. In this case the molecular weight of the polymer was also independent of the reaction conditions.

The data shown in Fig. 1 are plotted in Fig. 5 as if the reaction were first-order with respect to the monomer concentration. The reaction rates decreased with the reaction time and deviated from the first-order plots at the initial stage of the reaction, but later the relation between $\ln([M]_0/[M])$ and the reaction time became straight lines with the same slope at 0 and at 30°C.

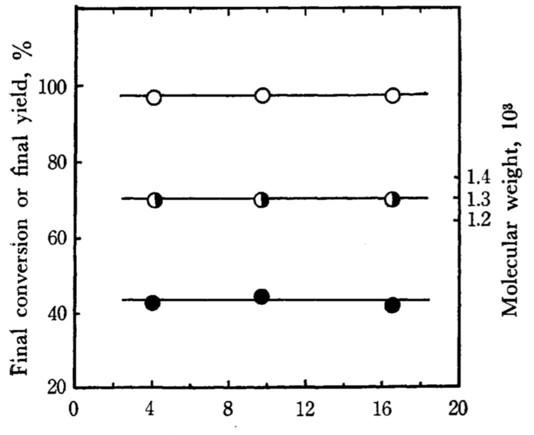


Fig. 3. Anionic polymerization of *trans*-β-methylstyrene by *n*-BuLi in THF.—Effect of initiator concentration

○: Final conversion

●: Final yield

◑: Molecular weight of methanol-insoluble polymer

$[M]_0$ 0.41 mol/*l*, Temp. 30°C, Time 48 hr

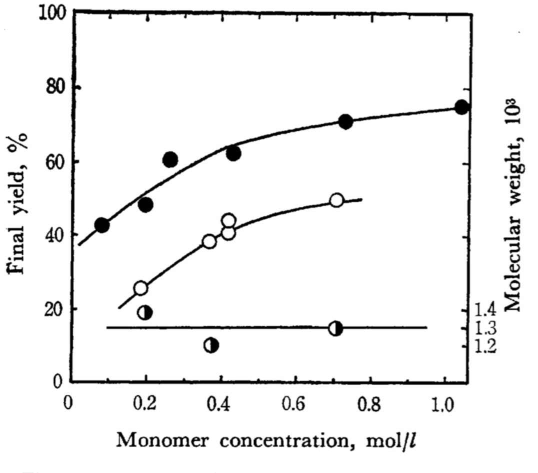


Fig. 4. Anionic polymerization of *trans*-β-methylstyrene by *n*-BuLi in THF.—Effect of monomer concentration.

●: Final yield at 0°C

○: Final yield at 30°C

◑: Molecular weight of polymer obtained at 30°C

[*n*-BuLi] 0.40×10^{-2} mol/*l*, Time 48 hr

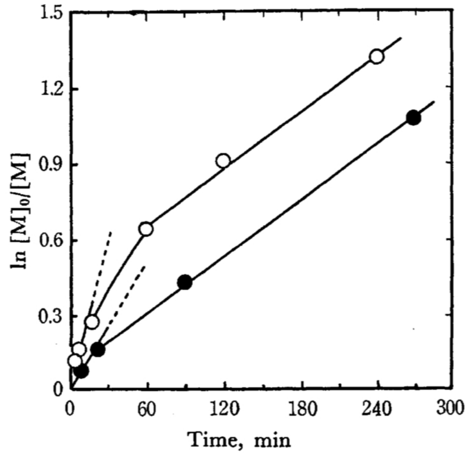


Fig. 5. Anionic polymerization of *trans*-β-methylstyrene by *n*-BuLi in THF.—First order plot of reaction rate.

●: At 0°C,

○: At 30°C,

$[M]_0$ 0.41 mol/*l*,

[*n*-BuLi] 4.5×10^{-3} mol/*l* at 0°C; 4.0×10^{-3} mol/*l* at 30°C

TABLE 2. TESTING OF EQUILIBRIUM IN THE POLYMERIZATION OF *trans*-β-METHYLSTYRENE IN TETRAHYDROFURAN

Solvent: THF, 20 m*l*; initiator: *n*-BuLi, 0.1 mmol

Monomer g	Temp. °C	Time hr	Conversion %
1.12	60	48	72
1.12+1.15[a)]	60	96	34[b)]
1.12	60 0	48 then 48	72

a) Added after 48 hr.

b) Against total monomer.

The existence of an equilibrium in the polymerization of *trans*-β-methylstyrene at 60°C was checked. The monomer was polymerized at 60°C; after the reaction had ceased, (1) a fresh monomer was added to the reaction mixture, or (2) the reaction mixture was cooled to 0°C and left to stand 48 hr at this temperature. As shown in Table 2, the conversion did not change from that in the original reaction mixture, indicating that there is no equilibrium in the reaction at 60°C.

Electronic Spectra of Reaction Mixtures. The electronic spectra of the solutions are shown in Fig. 6. The reactions were carried out between *trans*-β-methylstyrene and *n*-BuLi, and between allylbenzene and *n*-BuLi, in tetrahydrofuran. Curve A, with an absorption maximum at 340 mμ in Fig. 6, is the spectrum of the reaction product of *trans*-β-methylstyrene with an excess of *n*-BuLi at room temperature. Curve B shows the spectrum of the reaction product after 48 hr in the polymerization of *trans*-β-methylstyrene with *n*-BuLi at 0°C. It has an absorption maximum at 398 mμ. A very similar spectrum (Curve B′) was obtained from the reaction product between allylbenzene and an equimolar amount of *n*-BuLi at room temperature. At 60°C this spectrum shifted to Curve D, which has an absorption maximum at 570 mμ. When *trans*-β-methylstyrene was polymerized with *n*-BuLi at 60°C, after 48 hr the reaction mixture

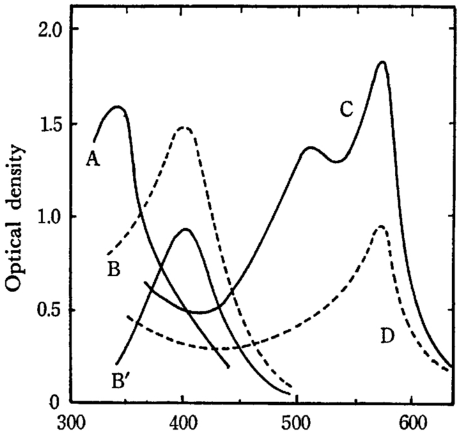


Fig. 6. Electronic spectra of anions in THF.

A: β-MeSt+excess *n*-BuLi, at room temp., after 5 min

B: Excess β-MeSt+*n*-BuLi, at 0°C, after 48 hr

B′: Allylbenzene+*n*-BuLi, at room temp., after 5 min

C: Excess β-MeSt+*n*-BuLi, at 60°C, after 48 hr

D: Allylbenzene+*n*-BuLi, at 60°C, after 48 hr

gave the spectrum shown as Curve C in Fig. 6. This spectrum contains two absorption maxima, at 510 and 570 mμ.

Structure of Polymer. The infrared spectrum of the methanol-insoluble polymer obtained at 30°C is shown in Fig. 7. As a whole the spectrum was very similar to that of polystyrene, except for the strong absorption bands at 2960, 2875, and 1377 cm^{-1} due to methyl groups and the extremely weakened band at 2925 cm^{-1} due to methylene groups. The IR-spectrum of the methanol-soluble fraction, which has an average molecular weight of 360, was just the same as that of the methanol-insoluble fraction, but it showed a strong absorption at 2925 cm^{-1}

The ultraviolet spectrum of the methanol-soluble and insoluble fractions showed no C_6H_5–CH=CH– structure, which may be expected to have a strong absorption at about 292 mμ due to the conjugation between a phenyl group and a C=C double bond.

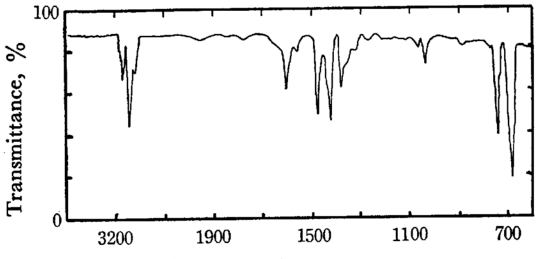


Fig. 7. Infrared spectrum of poly-β-methylstyrene (KBr).

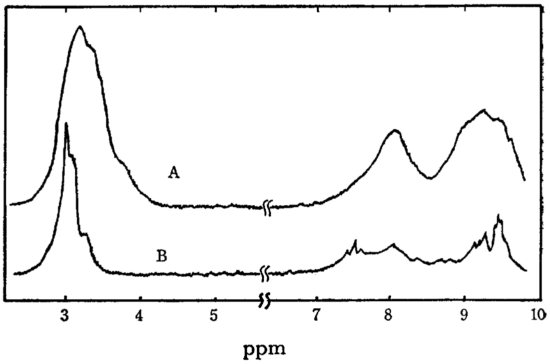


Fig. 8. NMR spectra of poly-β-methylstyrene.

A: Methanol-insoluble fraction

B: Methanol-soluble fraction

In Fig. 8 the NMR spectra of the methanol-insoluble and soluble polymers are shown. In neither the spectra was there any absorption at 3.5—5 ppm, where the signal of a proton attached to a C=C double bond appears. The spectrum of the methanol-insoluble polymer showed that the ratios of methyl to methylene protons and of phenyl to other protons were 3 : 2 and 5 : 5 respectively.

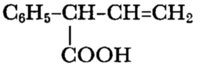
These results indicate that the polymer was formed by the usual addition polymerization at the C=C double bond, and that there is no essential difference between the structures of the methanol-soluble and -insoluble polymers.

Discussion

In spite of the long reaction time, the anionic polymerization of *trans*-β-methylstyrene in hydrocarbon solvents gave no polymer with a molecular weight high enough to be insoluble in methanol. However, the spectroscopic measurements showed that, compared with the amount of the initiator used, much of the monomer was consumed by the reaction, suggesting conversion to low-molecular-weight products.

Morton *et al.*[13] investigated the reaction between β-methylstyrene and *n*-amylsodium in *n*-pentane at room temperature. They reported that the carbonation of anions produced in the reaction gave mostly the I and II acids, but very small amounts of products with higher molecular weights.

C_6H_5-CH=CH-CH_2-COOH (I)



$C_6H_5\text{-}\underset{\displaystyle COOH}{\underset{|}{CH}}\text{-}CH{=}CH_2$ (II)

Pines *et al.*[14] also reported that the main product of the reaction between β-methylstyrene and metallic

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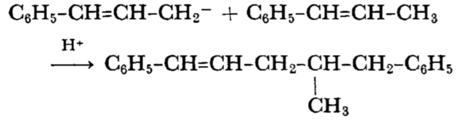
[13] A. A. Morton and E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **74**, 5437 (1952).

[14] H. Pines and J. Shabtai, *J. Org. Chem.*, **29**, 2408 (1964).

sodium in cyclohexane at 100°C was the following compound, III:

$$R^- + C_6H_5\text{-}CH{=}CH\text{-}CH_3 \longrightarrow RH + C_6H_5\text{-}CH{=}CH\text{-}CH_2^-$$



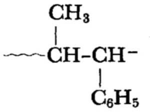
$$C_6H_5\text{-}CH{=}CH\text{-}CH_2^- + C_6H_5\text{-}CH{=}CH\text{-}CH_3 \xrightarrow{H^+} C_6H_5\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}C_6H_5$$

III

These results indicate that, in hydrocarbon solvents, carbanion does not attack the C=C double bond, but abstracts a proton from the methyl group of the monomer.

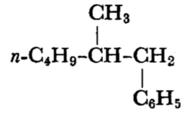
In tetrahydrofuran, *trans*-β-methylstyrene polymerizes to give a methanol-insoluble polymer as well as a soluble one; even in a non-polar solvent it gave the same polymers, though the amounts were small, in the presence of a small quantity of tetrahydrofuran (Table 1). The two polymers, methanol-soluble and -insoluble, were the same in their structure (*i. e.*, the polymers were formed by the usual addition polymerization at the C=C double bond), but they were different in molecular weight.

The structure of the polymer shows that the propagation reaction in the polymerization of *trans*-β-methylstyrene proceeds through the addition of a benzyl-type anion, IV, to the monomer. It has been known that benzyl-type anions have their absorption maxima at around 340 mμ.[12,15] Therefore, the absorption band at 340 mμ (Fig. 6, A) shown by the fresh reaction mixture between n-BuLi and *trans*-β-methylstyrene must be due to the benzyl-type anion. Herbranderson *et al.*[4] obtained Compounds V and VI, plus a small amount of high-molecular-weight materials, as the main products of the reaction between equimolar amounts of β-methylstyrene and n-BuLi in diethyl ether. These results indicate that, in a polar solvent, carbanion adds to the C=C double bond of β-methylstyrene rather than abstracts a proton of a methyl group in this monomer. The polymerization of *trans*-β-methylstyrene is an extreme example of solvent effects on the polymerizability of a monomer by an anionic mechanism.



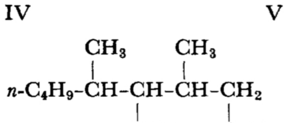
$$\sim\!\sim\underset{\displaystyle C_6H_5}{\overset{\displaystyle CH_3}{CH}}\text{-}\underset{\displaystyle C_6H_5}{CH^-}$$

IV



$$n\text{-}C_4H_9\text{-}\overset{\displaystyle CH_3}{CH}\text{-}\underset{\displaystyle C_6H_5}{CH_2}$$

V



$$n\text{-}C_4H_9\text{-}\overset{\displaystyle CH_3}{CH}\text{-}\underset{\displaystyle C_6H_5}{CH}\text{-}\overset{\displaystyle CH_3}{CH}\text{-}\underset{\displaystyle C_6H_5}{CH_2}$$

VI

In the anionic polymerization of *trans*-β-methylstyrene in tetrahydrofuran, the monomer can be completely consumed during a long reaction period at 0—30°C, although the rate is very slow compared with the polymerization of styrene. Szwarc *et al.*[5,17] found that the rate constant of the addition of living sodium polystyrene to β-methylstyrene was *ca.* 20 $l\,\mathrm{mol}^{-1}\,\mathrm{sec}^{-1}$ at 25°C in tetrahydrofuran, and that of the same anion to styrene, *ca.* 500 $l\,\mathrm{mol}^{-1}\cdot\mathrm{sec}^{-1}$, suggesting a smaller reactivity of β-methylstyrene.

The molecular weight of the polymer was independent of the yield, and of the concentrations of the monomer and the initiator, indicating a controlled chain growth by chain transfer to the monomer.

The absorption at 398 mμ (Fig. 6, B) observed in the reaction mixture at the later stage was that of the allyl anion, VII, which was also obtained by Waack *et al.*[12] in the reaction between allylbenzene and n-BuLi in tetrahydrofuran:

$$R^- + C_6H_5\text{-}CH{=}CH\text{-}CH_3 \longrightarrow C_6H_5\text{-}CH{=}CH\text{-}CH_2^- + RH$$

VII

The VII anion was produced by chain transfer to the monomer in the anionic polymerization of *trans*-β-methylstyrene in tetrahydrofruan, as is shown above. It is fairly stable and can exist at a concentration sufficient to be observed in the solution. Szwarc *et al.*[5] also observed the abstraction of a proton of the methyl group of β-methylstyrene by a polystyryl anion. Figure 6 shows that the anion, IV, produced at the initial stage of the reaction diminished, while the VII anion gradually appeared with time.

The average degree of polymerization of the methanol-insoluble polymer obtained at 0°C was about 15. Therefore, the chain-transfer constant ($=k_p/k_{tr}$) may be smaller than 15 at this temperature because of the presence of lower-molecular-weight products soluble in methanol. The decrease in the methanol-insoluble polymer at elevated reaction temperatures shows that the rate of the chain transfer increases with the elevation of the temperature more than that of the propagation does. The re-initiation by the allyl anion produced by the chain transfer reaction is considered to be rather slow because of the stability of the allyl anion. This slow re-initiation may be the cause of the retardation of the polymerization observed after the initial stage of the reaction.

The polymerization of *trans*-β-methylstyrene at 60°C gave only a low final conversion and no polymer insoluble in methanol, in spite of the presence of living anions, recognized by means of

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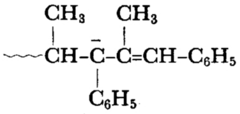
[15] S. Bywater, A. F. Johnson and D. J. Worsfold, *Can. J. Chem.*, **42**, 1225 (1964).

[16] R. Asami, M. Levy and M. Szwarc, *J. Chem. Soc.*, **1962**, 361.

[17] D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

the color. As the cause of the lower final conversion at an elevated temperature two mechanisms are possible: the equilibrium polymerization due to a low ceiling temperature, and the conversion of an active chain end to an inactive carbanion. The possibility of equilibrium polymerization can, however, be eliminated in view of the results shown in Table 2.

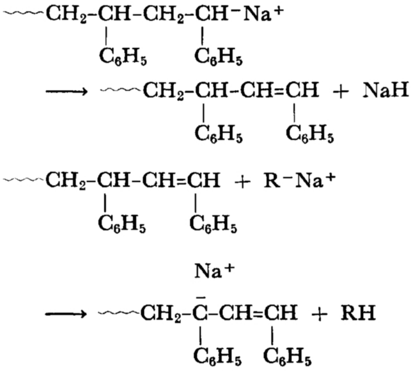
On the other hand, the production of unreactive carbanions was supported by spectroscopic measurements. The absorption at 510 mμ observed in the reaction at 60°C in tetrahydrofuran may be considered to be due to the VIII anion as follows:



$$\sim\overset{CH_3}{\overset{|}{C}}H-\underset{\underset{C_6H_5}{|}}{\overset{-}{C}}-\overset{CH_3}{\overset{|}{C}}=CH-C_6H_5$$

VIII

Szwarc *et al.*[16] have reported that the stable anion IX, with an absorption maximum at 535 mμ was produced in the polymerization of styrene by sodium in tetrahydrofuran:



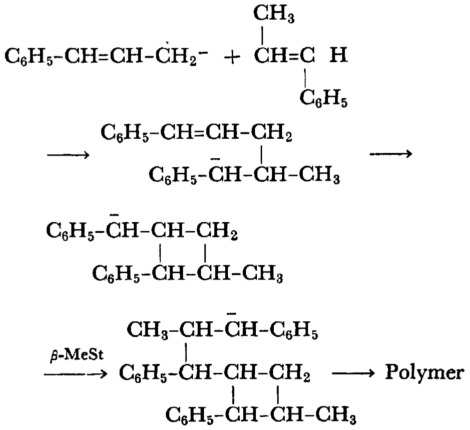
$$\sim CH_2-\underset{C_6H_5}{\underset{|}{C}}H-CH_2-\underset{C_6H_5}{\underset{|}{C}}H^-Na^+ \longrightarrow \sim CH_2-\underset{C_6H_5}{\underset{|}{C}}H-CH=\underset{C_6H_5}{\underset{|}{C}}H + NaH$$

$$\sim CH_2-\underset{C_6H_5}{\underset{|}{C}}H-CH=\underset{C_6H_5}{\underset{|}{C}}H + R^-Na^+ \longrightarrow \sim CH_2-\underset{C_6H_5}{\underset{|}{\overset{Na^+}{\overset{-}{C}}}}-CH=\underset{C_6H_5}{\underset{|}{C}}H + RH$$

IX

The anion VIII will be formed from poly-β-methylstyrene if a reaction similar to the above takes place. The anion will show then an absorption band at rather a lower wavelength than that of the anion IX. This may be caused by the lower conjugation between the C=C double bond and the benzene nuclei due to the steric hindrance of the methyl group. It is also known that a lithium counter ion lowers the λ_{max} of carbanion.[18] The structure of the other anion produced at 60°C and with a λ_{max} at 570 mμ is not certain at the present time, but it may be produced by the further change of the anion of allylbenzene VII. Both the anions with absorptions at 510 and 570 mμ are quite stable, as evidence by the fact that they could not initiate the polymerization of *trans*-β-methylstyrene. They could, however, cause the polymerizations of styrene and methyl methacrylate. The production of the anions is accelerated at higher temperatures.

The infrared and NMR spectra of the polymer showed that the monomer polymerizes by the normal addition polymerization mechanism. The chain transfer to the monomer produces the allyl anion VII, and so it may be expected that the polymer initiated by this anion will have a C=C double bond at the chain end. However, IR, UV, and NMR spectroscopies indicate that there is no aliphatic unsaturation, even in the low-molecular-weight polymer. The one possibility of the elimination of the double bond in the polymer is the following reaction:



$$C_6H_5-CH=CH-CH_2^- + \overset{CH_3}{\overset{|}{C}}H=\underset{C_6H_5}{\underset{|}{C}}\ H \longrightarrow \begin{array}{c} C_6H_5-CH=CH-CH_2 \\ \qquad\qquad | \\ C_6H_5-\overset{-}{C}H-CH-CH_3 \end{array} \longrightarrow$$

$$\begin{array}{c} C_6H_5-\overset{-}{C}H-CH-CH_2 \\ \qquad | \quad\ \ | \\ C_6H_5-CH-CH-CH_3 \end{array}$$

$$\xrightarrow{\beta\text{-MeSt}} \begin{array}{c} CH_3-CH-\overset{-}{C}H-C_6H_5 \\ | \qquad\qquad \\ C_6H_5-CH-CH-CH_2 \\ \quad | \quad\ \ | \\ C_6H_5-CH-CH-CH_3 \end{array} \longrightarrow \text{Polymer}$$

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[18] J. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).