Spectroscopic Study on the Living Polymers of Styrene, Butadiene and their Derivatives

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Recently the living polymers of styrene[1-3,5-7], its derivatives, butadiene[4] and isoprene have been an object of investigation, in view of their interesting property as an initiator of polymerization of vinyl monomers.

Their structure which seems to be the origin of the red color and the reactivity has been the subject of considerable discussion[1,2,5]. For the living polymer of styrene Szwarc proposed a structure of polymer anion having two groups of benzyl anion type at both ends of the polymer chain[2]. However, no direct evidence has been shown for this structure.

In the present paper, comparing the spectra of the living polymers of styrene and its derivatives with that of alkali benzyl, the

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[1] G. Meshitsuka and Y. Okada, *Chemistry of High Polymers* (*Kobunshi-kagaku*), **14**, 33, 37, 123 (1957).

[2] M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2655 (1956); M. Szwarc, *Nature*, **178**, 1168 (1956).

[3] R. Wack, A. Rembaum, J. D. Coombes and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 2026 (1957).

[4] H. Brody, M. Ladacki, R. Milkovitch and M. Szwarc, *J. Polymer Sci.*, **25**, 221 (1957).

[5] K. Hirota, K. Kuwata, H. Togawa and S. Ishida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 602 (1958).

[6] K. Hirota, K. Kuwata and K. Morigaki, This Bulletin, **31**, 538 (1958); **32**, 100 (1959).

[7] K. Hirota and K. Kuwata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1421 (1957); K. Kuwata and K. Hirota, *Annual Reports of the Institute for Fibre Research* (*Sen-i Kagaku Kenkyu-jo Nen-po*), **11**, 20 (1958).

author is to report that their structure is a polymer anion with the end of benzyl anion type.

The existence of the living polymers of butadiene and isoprene was asserted by Szwarc et al.[4] In this paper, their structure and reactivity are to be discussed from the spectroscopic data on the living polymers prepared by the direct reaction of butadiene and isoprene with metallic sodium, and on the block polymerization of isoprene with the living polymers of styrene.

Experimental

Materials Used.—Since the living polymers have an extreme reactivity toward water, oxygen, and carbon dioxide, special precautions on purifications of the starting materials are required[5,7]. In addition to the ordinary method of purification the monomers (styrene, α-methyl styrene, p-methyl styrene and p-divinyl benzene) were dried over metallic sodium for several hours and then distilled into storage vessels under reduced pressure. The solvents, tetrahydrofuran (THF), dioxane and toluene, were refluxed over metallic sodium or potassium for several hours, and also distilled under reduced pressure into a glass ampoul containing a piece of sodium and a small amount of anthracene. The blue color appeared instantly and stayed permanently. The solvents were distilled under reduced pressure into the reaction vessel as required. For toluene, however, styrene was used instead of anthracene, since toluene is a poor solvent for sodium adduct of anthracene. Mercury dibenzyl, prepared by the Grignard reaction[8] between benzylmagnesium chloride with mercuric chloride, was purified by recrystallization from toluene. Diallyl ether of GR grade, dried over metallic sodium for a short time, was purified by distillation under reduced pressure.

Preparation of the Samples.—All the processes of preparations and measurements were carried out in the glass vessels which were previously degassed as much as possible. A typical method of preparation was as follows: Alkali metal was distilled under reduced pressure from an ampoul A into an ampoul B (see Fig. 1). Monomer or solvent was distilled into B from an ampoul C. Then the vessel was sealed off from the vacuum system. The reaction proceeded gradually and an intensely colored solution of the living polymer formed. This solution was filtered through a glass filter G and stored in an ampoul D. The solution of the living polymer or the anion formed was poured into the measuring cell E and was diluted by the solvent distilled from D until an appropriate concentration was obtained. The concentration of the living polymers of styrene and isoprene were determined by the flame spectroscopy of alkali metal contained in the solutions, and the molar extinction coefficients of the living polymers were estimated.

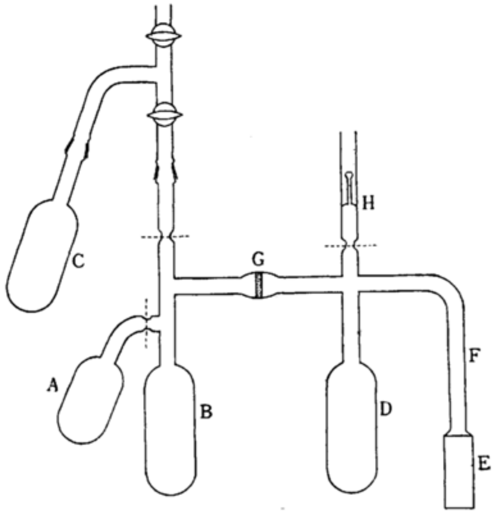

Fig. 1. Apparatus for preparation of the living polymers.
A, B, C and D: Glass ampoul, E: quartz cell, F: Gradual joint, G: Glass filter, H: Breakable joint.

Measurement of Absorption Spectra. — Absorption spectra of the living polymers and the anions were measured from 300 mμ to 2 μ with a Beckman DU type spectrophotometer equipped with an additional cover on the cell holder. After the measurement of the spectra, the vacuum was broken off and the spectra of the product were again measured.

Experimental Results

A spectrum between 300 mμ and 2 μ for the toluene solution of the living polymer of styrene is shown in Fig. 2. In addition to the characteristic absorption at 510 mμ which had already been reported[1,5] another absorption at 450 mμ and an end absorption at longer wavelength were also observed. On the THF and dioxane solutions the absorptions were observed at 520 and 535 mμ respectively, shifting

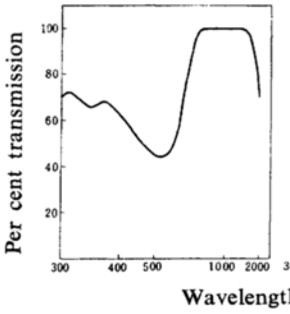

Fig. 2. Spectrum of the toluene solution of the living polymer of styrene.

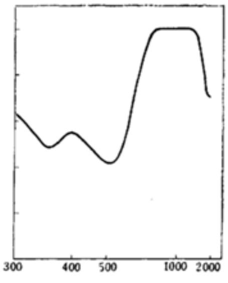

Fig. 3. Spectrum of the THF solution of benzyl anion sodium.

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[8] P. Wolff, *Ber.*, **46**, 64 (1913).

toward longer wavelength according as the solutions were diluted.

The near infrared spectrum for the filmy state of the living polymer of styrene from 2 to 3.5 μ was the same as that of polystyrene, but its intensity was stronger than that of "dead polymer"[*] throughout this region. Therefore a very broad absorption in this region may exist. In the cases of the living polymers of styrene with potassium, rubidium and cesium in toluene solution, the corresponding absorptions were observed at 518, 525 and 535 mμ respectively.

For the living polymer of 1, 1-diphenyl ethylene in THF solution, the absorption at 525 mμ and two other absorption at 450 mμ and the end one at longer wavelength were also observed.

In cases of α-methyl styrene and *p*-methyl styrene of toluene solution the absorption at 515 mμ was observed in addition to two other absorptions.

The absorptions at 550 and 1650 mμ were observed in case of divinyl benzene, and the latter seems to correspond to the end absorptions at longer wavelength for the living polymers of styrene etc.

A spectrum of the red THF solution of alkali benzyl is shown in Fig. 3. A maximum absorption which is characteristic of alkali benzyl at 505 mμ was observed in addition to two other absorptions. The shift of the maximum absorption at 505 mμ which originated from the alteration of alkali metal was very small. This absorption obeyed the law of Beer-Lambert within a concentration range of $10^{-2}\sim 10^{-3}$ moles per litre.

Isoprene and butadiene reacted with sodium film, forming yellow adducts of high molecular weight. Dissolving these adducts into THF, slightly yellow and very reactive solutions were obtained. These solutions showed the maximum absorptions at 375 and 357 mμ respectively, and could initiate the polymerization of styrene and isoprene. These absorptions quickly disappeared upon exposure to air. A spectrum for the living polymer of isoprene in THF solution is shown in Fig. 4.

A yellow solution of allyl sodium containing sodium allylate, which was a byproduct[9] of the reaction, had a maximum absorption at 375 mμ and an end absorption at longer wavelength as shown in Fig. 5. The maximum absorption at 375 mμ was unaltered on dilution within the concentration range of $10^{-2}\sim 10^{-3}$ moles per litre.

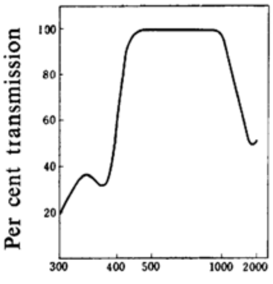

Fig. 4. Spectrum of the THF solution of the living polymer of isoprene.

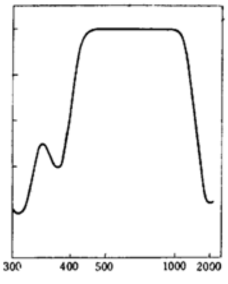

Fig. 5. Spectrum of the THF solution of allyl sodium.

Block polymerization of isoprene with styrene was carried out, by use of the living polymer of styrene as the initiator, as follows: A constant amount of purified isoprene monomer was added by distillation through a breakable joint into the THF solution of styrene living polymer contained in ampoul D (Fig. 1). The absorption at 510 mμ of the living polymer of styrene (Fig. 6a) decreased by addition of isoprene and the absorption at 375 mμ of the living polymer of isoprene appeared as shown in Fig. 6b. The latter increased by further addition of isoprene as shown in Fig. 6c.

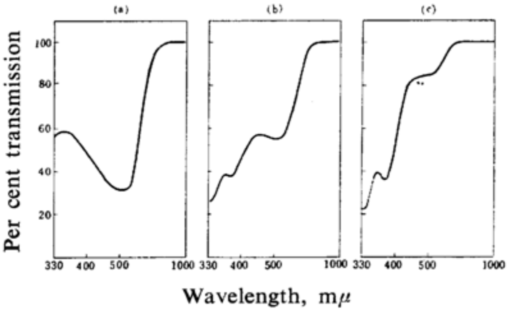

Fig. 6. Change of spectrum in the block polymerization of isoprene by the living polymer of styrene.

Discussion

Absorption Spectra of Benzyl Anion Type.— Since the two maximum absorptions and the end absorption observed for the living polymer of styrene disappeared quickly upon exposure to air, they seem to be characteristic of the living polymer. However, when the starting materials used were not perfectly purified, yellow solutions were obtained. They had the maximum absorption only at 430 mμ besides the end absorption, and could not initiate polymerization. These two absorptions, therefore, may have originated from the decomposition product of the living polymer.

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[*] The reaction product of the living polymer with air, and such product has no more reactivity to initiate the polymerization of styrene etc.

[9] R. L. Letsinger and J. G. Traynham, *J. Am. Chem. Soc.*, **70**, 3342 (1948).

It seems that the temperature dependence of the absorption at 510 mμ of the living polymer of styrene may indicate the behaviour of association, but further study is necessary to confirm the conjecture.

The other absorption at 510 mμ, which may be a characteristic measure of the living polymer of styrene varied according as the kind of alkali metal was altered. The intermolecular charge-transfer spectra shown by a large number of molecular complexes in solution were found to exhibit certain regularities in regard to wavelength$^{10)}$. The wavelength of these transitions shows an excellent correlation i. e. a linear relation between frequency ν and ionization potential I_p of the electron donor partners of the complexes :

$$h\nu = 0.61 I_p - 1.8 \text{ (in eV.)}$$

In case of the living polymer of styrene, the similar relation seems to exist as shown in Fig. 7, but the decrease of wavelength with the increase of ionization potential was small as compared with those of the molecular complexes, and also no donor-acceptor complexes such as a type containing alkali metal as the donor or aromatic hydrocarbon as the acceptor has been known. The change of absorption, therefore, would be caused by the change of solvation or dissociation of the polymer anion.

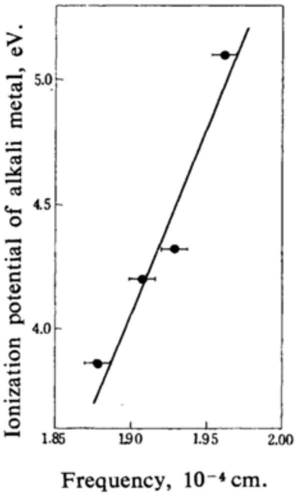

Fig. 7. Ionization potential of alkali metal versus the frequency of the absorption maximum.

Considering the facts that the position of the maximum absorption near 505 mμ of THF solution of benzyl sodium is constant on dilution and that ether solution of benzyl sodium is conductive as shown by previous investigators$^{11)}$, it is believed that alkali benzyl in dilute THF solution is completely ionized. The absorption curve of alkali benzyl is the same as that of the living polymer of styrene. It seems evident, therefore, that the end group of benzyl anion type exists in the solution.

The theoretical investigations on the electronic states of benzyl anion and allyl anion were already carried out by several researchers$^{12-14)}$. Theoretically calculated wavelength of absorption for benzyl anion, shown in Table I are shorter than that of the observed absorption. The cause of this difference is partly due to the solvation of anion, but this effect may not be so much. Therefore,

TABLE I. MAXIMUM ABSORPTION OF THE LIVING POLYMERS, ALKALI BENZYL AND ALLYL SODIUM

	Living polymer of styrene with sodium	Alkali benzyl			Living polymer of butadiene with sodium	Living polymer of isoprene with sodium	Allyl sodium
		Sodium	Potassium	Rubidium			
Wavelength(mμ) obs.	510(530)	510	512	515	357	375	375
Wavelength(mμ) theor.	464 (transition $^1A_1-^1B_1$)$^{b)}$				326$^{c)}$, 250$^{a)}$ (transition $^1A_1-^1B_1$)		
Extinction coeff. obs.	1.9×10^3	—	—	—	—	3.2×10^2	
Oscilator strength theor.	0.43				0.036		

a) Chalvet$^{16)}$, b) Longuet-Higgins and Pople$^{15)}$, c) corrected value.

TABLE II. MAXIMUM ABSORPTIONS OF THE LIVING POLYMERS OF STYRENE AND ITS DERIVATIVES

	Styrene	α-Methyl styrene	p-Methyl styrene	Divinyl benzene	1,1-Diphenyl ethylene
Wavelength(mμ) (λ) obs.	510($=\lambda_s$)	515	515	550	525
λ/λ_s obs.	1.00	1.01	1.01	1.08	1.03
λ/λ_s theor.	1.00	1.01	1.01	1.04	1.00

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10) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

11) W. Schlenk, *Ber.*, **50**, 262 (1917).

12) W. Bingel, *Z. für Naturforschung*, **10a**, 463 (1955).

13) H. G. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, (*London*), **A68**, 591 (1955).

14) O. Chalvet, *Comt. rend.*, **234**, 2369 (1952).

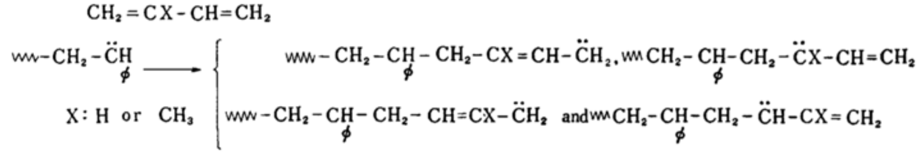
it may be attributed to oversimplification of the theory or to inadequate estimation of the electron interaction integrals used, as will be discussed later in the case of allyl anion.

The small difference of the absorption maximum between the solution of alkali benzyl and the living polymer of styrene may be ascribed to the effect of substitution of α-hydrogen of benzyl anion by the polymer chain of polystyrene, since no difference was observed between the solution of alkali benzyl-polystyrene mixture and that of alkali benzyl.

As an effect of substitutions in anionic group of the living polymer of styrene, it was observed that the maximum absorption shifted toward a longer wavelength as the π-electronic conjugation in anionic group became larger. This effect was approximately interpreted by the Hückel treatment on the π-electronic structure of the anions as shown in Table II.

Absorption Spectra of Allyl Anion Type.—By comparing the maximum absorptions of the living polymers of butadiene and isoprene at 375 and 357 mμ with that of allyl sodium, they seem to be characteristic of allyl anion. Extinction coefficient of the absorption for the living polymer of isoprene was the order of 3×10^3 corresponding to the calculated oscillator strength of the order of 0.036 for allyl anion. Two other absorptions for the solution of the living polymers and that of anion may be attributed to the decomposition product or the byproduct. A typical value[14] of the longest wavelength calculated semi-empirically for allyl anion is shown in Table I, where considerable discrepancies between calculated and experimental values exist. This may be ascribed to the solvation of the anion in solution to some extent, but should rather be attributed to other causes: for example, rough approximation in the theory or inadequate estimation of the integrals used. If the Coulomb electronic repulsion integral for the two electrons on adjacent two carbon atoms in the method of Pople or of Pariser and Parr is decreased, a better approach to the observed value will be obtained*. Such a correction seems to be reasonable since the abnormally partial distribution of electronic charge, which resulted from the calculation, diminishes at the same time. A value corrected on this line is listed in Table I, showing that the partial distribution of charge diminishes to that of the Hückel method. It may be reasonable to consider that the structure of the living polymers of butadiene and isoprene are the polymer anion having the group of allyl anion type at the end of a polymer chain.

Both benzyl sodium and allyl sodium were known to have a reactivity as the initiators of polymerization of styrene[15] etc. Therefore, it may be plausible to attribute the reactivity of the living polymers to their anionic groups. Such a presumption was justified by the change of spectrum for the living polymer of styrene to that for isoprene, in the block polymerization of isoprene by the use of the living polymer of styrene as the initiator; the alteration of end group of benzyl anion type with that of allyl anion type may occur as follows:



$$\sim\!\!-CH_2-\underset{\phi}{\ddot{C}H}\xrightarrow{CH_2=CX-CH=CH_2}\left\{\begin{array}{l}\sim\!\!-CH_2-\underset{\phi}{CH}-CH_2-CX=CH-\ddot{C}H_2,\ \sim\!CH_2-\underset{\phi}{CH}-CH_2-\ddot{C}X-CH=CH_2\\ \sim\!\!-CH_2-\underset{\phi}{CH}-CH_2-CH=CX-\ddot{C}H_2\ \text{and}\sim\!CH_2-\underset{\phi}{CH}-CH_2-\ddot{C}H-CX=CH_2\end{array}\right.$$

$X:H$ or CH_3

Mechanism of Polymerization.—The existence of the radical anion of styrene and its derivatives in the living polymers of low molecular weight was shown by the paramagnetic resonance absorption measurements[6,17]. Then the first step of the polymerization of styrene and its derivatives may be the formation of the radical anion which can play the role of the initiator of polymerization. The next step is the successive addition of monomers to the radical anion which will convert into the polymer anion making the polymerization reaction proceed. The end groups of radical type did not remain in the solution of the living polymers except the relatively stable diphenylmethyl radical type formed from the radical anion of 1, 1-diphenyl ethylene[16,17]. The general reaction scheme may be as follows:

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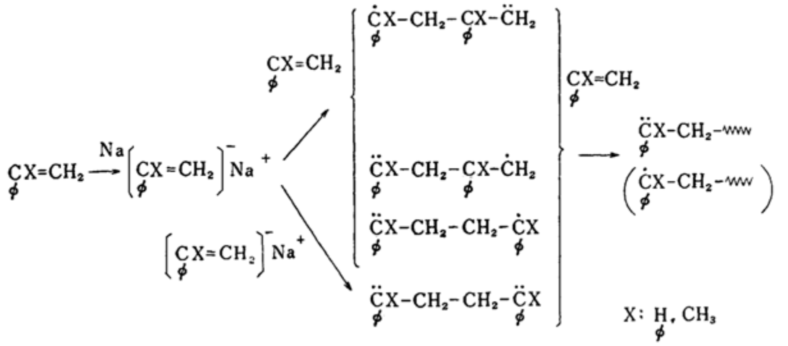
* Since the electronegativities of the carbon atoms of the anions should be different from these of the neutral molecule, the correction on this line is also necessary.

15) A. A. Morton, *J. Am. Chem. Soc.*, **68**, 93 (1946).

16) K. Kuwata, K. Morigaki, K. Hirota and J. Itoh, *Annual Reports of the Institute for Fibre Research* (*Sen-i Kagaku Kenkyu-jo Nen-po*), **12**, 9 (1959).

17) K. Kuwata, S. Ishida and K. Hirota, *J. Chem. Soc. Japan Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 25 (1959).



This scheme is more general than that of Szwarc, because the formation of radical anions is considered in addition to the bivalent dimer anion proposed by Szwarc.

In cases of butadiene and isoprene the situation is the same, but the existence of monomer radical anion has been confirmed experimentally only with isoprene[18].

Summary

The absorption spectra of the living polymers of styrene and its derivatives as well as of alkali benzyl have been measured from near infrared region to near ultra violet region, and they were compared. It has been concluded that these living polymers are the polymer anions having the groups of benzyl anion type at the end of a polymer chain.

The living polymers of butadiene and isoprene have been separated as the intermediates of polymerization by metallic sodium, and their spectra have been measured. Comparing these spectra with that of allyl sodium, it has been concluded that the living polymer of butadiene and isoprene are the polymer anions having the groups of allyl anion type at the end of a polymer chain. The spectroscopic study on the block polymerization of isoprene with the living polymer of styrene has been carried out. The mechanism of polymerization has been discussed.

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[18] K. Kuwata, K. Morigaki and K. Hirota, This Bulletin, 32, 895 (1959).