59. *Spontaneous Slow Transformations in the " Living " Polystyrene System.*

By G. Spach, M. Levy, and M. Szwarc.

The spontaneous slow spectral change of solutions of " living " polystyrene is shown to result from two consecutive reactions:

$$\sim\!\sim\!\sim CH_2{\cdot}CHPh^-Na^+ \longrightarrow \sim\!\sim\!\sim CH{=}CHPh + NaH$$

$$CH_2{\cdot}CHPh^-Na^+ + CHPh{=}CH{\cdot}CHPh{\cdot}CH_2\sim\!\sim\!\sim \longrightarrow \sim\!\sim\!\sim CH_2{\cdot}CH_2Ph + Na^+CHPh{=}CH{\cdot}CPh^-{\cdot}CH_2\sim\!\sim\!\sim$$

the first being rate-determining. This mechanism accounts for the dependence of the rate on the nature of the solvent, dilution, and degree of polymerization of the polymer.

The spectrum of the final product is that of 1,3-diphenylallyl negative ion, and its stability deprives the polymer of its ability to grow.

On addition of water, the polymeric allyl ion forms a polystyrene possessing a double bond in its chain. Such a polymer reacts with the alkali metal, re-forming the coloured allyl ion. This reaction may be used for qualitative and quantitative analyses of C=C bonds in polystyrene.

On storage solutions of " living " polystyrene undergo changes[1] which manifest themselves in their spectra as shown in Fig. 1. The 340 mμ peak, characteristic of the $\sim\!\sim\!\sim CHPh^-Na^+$ end-groups,* gradually disappears and a new peak appears in the region of 535 mμ together with some weaker bands at ~440 and ~610 mμ. The existence of an isosbestic point indicates constant stoicheiometry of the process and the absence of further consecutive reactions.

Most of these experiments were performed with tetrahydrofuran solutions; however, similar spectral changes were observed with benzene and dimethoxyethane solutions. The process in benzene was much slower than that in tetrahydrofuran; that in dimethoxyethane was very fast. No systematic attempt has been made to determine the kinetics of this change, but qualitative observations have shown that the reaction is faster when the molecular weight of the polymer is low.

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* See also *J.*, 1961, **361**, by Asami, Levy, and Szwarc.

[1] Levy, Szwarc, Bywater, and Worsfold, *Polymer*, 1960, **1**, 515.

The behaviour of " living " poly-α-methylstyrene differs from that of " living " polystyrene. Solutions of the former polymer appear to be stable and no changes of their spectrum have been observed. This seems to indicate that the α-hydrogen of polystyrene is involved.

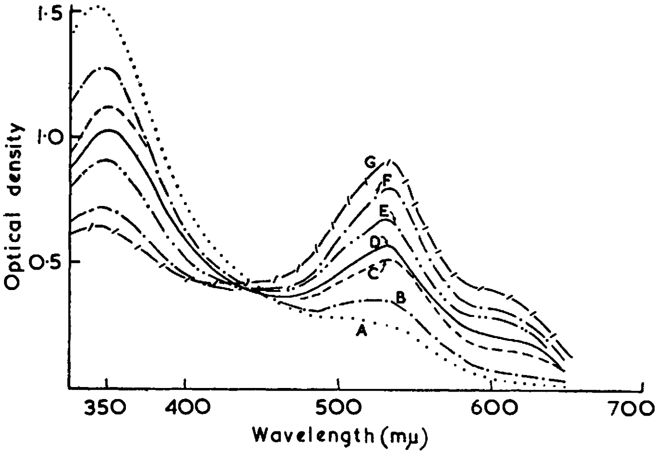


FIG. 1. " Isomerization " of " living " polystyrene of low molecular weight. Time (hr.): A, 0; B, 4·5; C, 29; D, 49; E, 97; F, 222; G, 318.

RESULTS

Characterization of the Polymers.—We have examined the original polystyrene and the polymer obtained from it after prolonged storage. We refer to the latter as " isomerized " polystyrene, denoting the original product as the " non-isomerized " one. Three samples, described in the Table, were used. Samples M-19 and M-27 were analyzed before and after " isomerization " and it was found that the concentration of the organometallic compound, which was determined by titration with methyl iodide, did not change in the process. This indicates that the investigated reaction does not involve solvent, *e.g.*, cleavage of tetrahydrofuran into alkoxide.

The non-isomerized and the isomerized " living " polystyrene were terminated with water and the spectra of the resulting polymers examined. The infrared spectra of the isomerized polymers in carbon tetrachloride differed only slightly from those of the original ones. For example, on isomerization sample M-36 showed a new band at 955 cm.$^{-1}$ which is characteristic of the $-CH=CH-$ group. Usually this also causes absorption at 1650 cm.$^{-1}$, but this band was not shown in the M-36 spectrum. In addition, new peaks were noticed at ~2950, 1450, and 1370 cm.$^{-1}$, whose significance is not obvious; probably they indicate the presence of a $C-CH_3$ group in the polymer (see discussion below).

In the ultraviolet spectra of sample M-19 in tetrahydrofuran (Fig. 2) the optical densities of the bands in the regions 255 and 269 mμ increased greatly on isomerization and two weaker bands appeared, at 285 and 294 mμ. These findings strongly suggest that a C=C double bond conjugated to a phenyl group is formed in the overall process. The extinction coefficient of this conjugated system at $\lambda_{max.}$ 255 mμ was estimated from the observed optical density to be 14,000—28,000, depending whether one or two $-C=CPh-$ groups are present in each 14-mer.

Characteristic of the polystyrenes used.

Sample *	$\overline{DP}$ †	Concn. (10^{-2}M) of alkali ion in original polymer	Method of " isomerization "
M-19	14	1·2	Left at room temp. No contact with alkali metal
M-27	5	1·9	
M-36	~3	35	Kept over Na–K alloy at room temperature

* Prepared in tetrahydrofuran. † Average degree of polymerisation.

This value compares favourably with the corresponding extinction coefficient of α- or β-methylstyrene (ε 11,500 is reported for the α- and 17,000 for the β-isomer).

To substantiate our conclusions we prepared 1,3-diphenylbut-1-ene by dimerizing styrene with sulphuric acid (this reaction was described by Stobbe and Posnjak,[2] and the structure of the product established by Stoermer and Kootz [3]). The ultraviolet spectrum of the diphenylbutene was described by Grumez [4] and confirmed by our studies. It shows a band at 253 mμ (ε 17,000) and two weaker bands at 285 and 293 mμ. The similarity of the spectrum of the diphenylbutene (the dimer) to that of the water-terminated isomerized polystyrene provides, therefore, a strong evidence for the presence of a C=C bond in the latter, although the band at 269 mμ shown by the polymer appears only as a shoulder in the dimer.

The infrared spectrum of the dimer also agrees well with the corresponding spectrum of the isomerized polymer. In particular, the band at 955 cm.$^{-1}$ is distinct, its intensity being of course much larger than for the polymer. The 1650 cm.$^{-1}$ band has a very low intensity, and thus its absence in the polymer spectrum is not surprising. The 2950, 1450, and 1370 cm.$^{-1}$ bands are clearly shown in the spectrum of the dimer, which is consistent with the presence of a methyl group in this compound. It seems, therefore, that at least some polymeric molecules present in our sample contain methyl groups. We believe that they might arise from the reaction of sodium hydride with free styrene, which is always present in the system,* followed by polymerization. As will be shown below, it is evident that sodium hydride is formed in the process investigated.

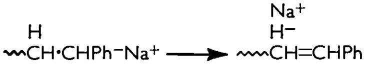
Formation of the C=C *Double Bond.*—The following mechanism is proposed to account for formation of the double bond:

$$\sim\!\sim CH_2{\cdot}CHPh^-Na^+ \longrightarrow \sim\!\sim CH{=}CHPh + NaH$$

This mechanism is supported by the subsequent observations: (1) No hydrogen gas was produced in the process when a sample of non-isomerized " living " M-27 polymer was kept for a few days in a sealed ampoule. During this period the transformation was complete, as shown by the ultraviolet spectrum. (2) Addition of water to a solution of " non-isomerized " polystyrene produced a negligible amount of hydrogen which, we believe, resulted from the presence of a small amount of " isomerized " polymer in the sample. After completion of the transformation addition of water produced a substantial amount of hydrogen, one-third to a half of that stoicheiometrically expected for the total amount of alkali. However, another sample obtained from a polymer of higher molecular weight produced no gas on addition of water. It is possible that the sodium hydride originally formed reacted with the free styrene (see above), and since the investigated process is slower for a polymer of higher molecular weight this reaction of sodium hydride could proceed to completion. (3) Addition of deuterium oxide to the isomerized polymer produced a gas which proved in a mass-spectrograph to be about 90% deuterium hydride, indicating that the hydrogen comes from sodium hydride: molecular deuterium, D_2, would be expected if metallic sodium was originally present or was formed in the process.

The formation of sodium hydride removes a negative charge from a polymer which possesses two negative charges, one at each end. The repulsion between these charges should facilitate this removal, and therefore the lower the molecular weight of the polymer the faster should be the reaction. Indeed, a dimer or trimer is substantially " isomerized " in a day or two, while a polymer of high molecular weight shows a visible change only after a week.

It was also observed that the investigated process is faster on dilution of the polymer solution. Since the reaction requires an approach of Na$^+$ ion to the β-hydrogen,



$$\sim\!\sim \overset{H}{C}H{\cdot}CHPh^-Na^+ \longrightarrow \sim\!\sim \overset{\overset{Na^+}{H^-}}{C}H{=}CHPh$$

the ease of dissociation of the ion-pair and the mobility of the Na$^+$ ions might be factors which accelerate the process. This explains the effect of dilution, as well as the acceleration of the process in ethers compared with the rate in benzene.

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* " Living " polymers must be in equilibrium with their monomers (see, *e.g.*, ref. 5).

[2] Stobbe and Posnjak, *Annalen*, 1909, **371**, 287.

[3] Stoermer and Kootz, *Ber.*, 1928, **61**, 2330; see also Marion, *Canad. J. Res.*, 1938, **16**, *B*, 213.

[4] Grumez, *Ann. Chim.* (*France*), 1938, **10**, 378.

[5] Szwarc, *Makromol. Chem.*, 1960, **35**, 132.

Reaction of Polymers containing Terminal C=C *Bonds.*—Polymers with the C=C end-group possess a relatively acidic hydrogen which may be transferred to the carbanion of the non-isomerized polymer:

$$\sim\sim\mathrm{CHPh{\cdot}CH{:}CHPh} + {}^{-}\mathrm{CHPh{\cdot}CH_2}\sim\sim \longrightarrow \sim\sim\bar{\mathrm{C}}\mathrm{HPh{\cdot}CH{:}CHPh} + \mathrm{Ph{\cdot}CH_2{\cdot}CH_2}\sim\sim$$

The 1,3-diphenylallyl anion produced by this reaction is probably responsible for the absorption at 535 mμ characterizing the isomerized polymer. Its formation should cause a shift towards longer wavelength in the absorption, as is observed, and its stability is responsible for its inability to initiate further polymerization of styrene. This hypothesis is supported by the observations of other workers [6] who found, *e.g.*, that cumylpotassium abstracts a proton from $\mathrm{Ph_2C{=}CH{\cdot}CH_2Ph}$, producing the $\mathrm{Ph_2C{=}CH{\cdot}CHPh^-}$ ion. However, more direct and conclusive evidence for the proposed reaction was obtained by treating the "living" non-isomerized polystyrene with the styrene dimer described above. The colour changed immediately, and the spectrum of the resulting solution was closely similar to that of the isomerized polymer (see Fig. 3). This indicates the occurence of the reaction:

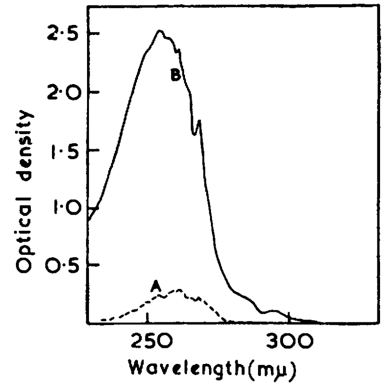

FIG. 2. Ultraviolet spectra of (A) non-"isomerized" and (B) isomerized polystyrene. Concn. of polymer 1·15 × 10^{-3}M. Concn. of C=C 1—2 × 10^{-4}M. These polymers were terminated by water.

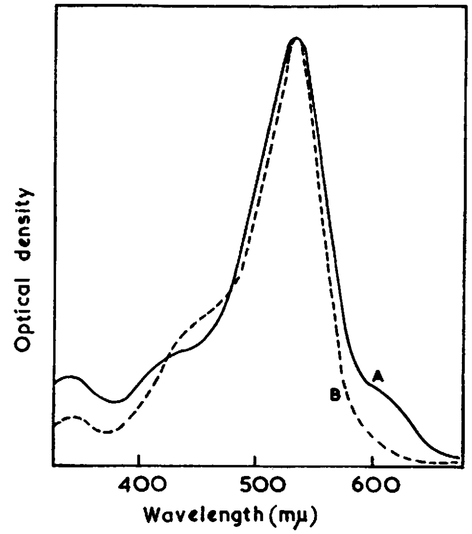

FIG. 3. Spectra of (A) "isomerized" polystyrene and (B) 1,3-diphenylbut-1-ene *plus* "living" polystyrene (counter-ion K^+). (The optical densities refer to arbitrary concentrations and were so that the two peaks coincide.)

$$\mathrm{CH_3{\cdot}CHPh{\cdot}CH{=}CHPh} + \sim\sim\mathrm{CH_2{\cdot}CHPh^-Na^+} \longrightarrow \mathrm{CH_3{\cdot}CPh^-{\cdot}CH{=}CHPh\ Na^+} + \sim\sim\mathrm{CH_2{\cdot}CH_2Ph}$$

The same result was obtained when "living" poly-α-methylstyrene was substituted for "living" polystyrene.

Further proof of the nature of the new coloured species was obtained from studies of polymers produced from the non-isomerized and isomerized "living" polystyrenes by deuterium oxide. The expected aliphatic C–D stretching band appeared at 2140 $\mathrm{cm.^{-1}}$ in the infrared spectrum of the non-isomerized M-36 polymer, confirming the structure of the "living" end; in the isomerized sample the intensity of this band dropped to about half its original value, as expected. Moreover, this decrease was not accompanied by the appearance of the corresponding aromatic C–D stretching band. The lack of the aromatic C–D absorption was ascertained by examining

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[6] Ziegler, Croessmann, Kleiner, and Schaefer, *Annalen*, 1929, **473**, 1.

the 13—17 μ region (potassium bromide prism). Tiers[7] showed that strong absorption should be observed in this region if deuterated phenyls are present. We therefore assume that the transformation process does not convert a benzyl anion into a phenyl anion, but involves proton transfer from the polymer possessing a C=C bond to the non-isomerized " living " polystyrene.

The proposed mechanism assumed that the new spectral band ($\lambda_{\text{max.}}$ 535 mμ) results from the presence in the polymeric chain of the 1,3-diphenylallyl anion. Such a species cannot be formed from " living " poly-α-methylstyrene as this lacks the pertinent hydrogen. Moreover, the optical density of the original absorption peak of " living " poly-α-methylstyrene does not change on storage. It appears, therefore, that the β-hydrogen atoms of this polymer are shielded and so no sodium hydride is formed.

Our assumption that some termination of non-isomerized " living " polymers takes place by proton transfer from isomerized polymers does not contradict the observation that apparently no organometallic compound was lost in the process. The titration of the organometallic compound was accomplished with methyl iodide. Since sodium hydride reacts with this reagent the titration gives the same value for the original and for the final solution.

Regenerated Polymers.—As the isomerized " living " polystyrene on reaction with water produces a polymer containing, in its chain, C=C bonds conjugated with phenyl groups, such polymers should react with alkali metals and produce coloured negative ions. This indeed is the case. The isomerized " living " polystyrene was terminated with water. The polymer was precipitated, dried, and redissolved in tetrahydrofuran. The solution was treated with metallic potassium: the colour developed rapidly. The absorption spectrum of this solution was identical with that of the isomerized polymer but the intensity indicated that the concentration of the coloured species was approximately half that present in the original solution. A similar experiment with the non-isomerized polymer failed to produce any colour.

It appears that electron-transfer produces the respective radical ions and eventually the " living " polymers[5] (probably by dimerization of the initial radical-ions). The latter react in turn with the polymers containing the intact C=C bonds, abstract the acidic protons, and form the 1,3-diphenylallyl negative ions. Since no hydrogen is formed on addition of water to the regenerated polymer sodium hydride is not formed in the process.

A similar reaction with the dimer (1,3-diphenylbut-1-ene) and potassium resulted in a solution which has the characteristic spectrum of the isomerized polymer.

It is essential to mention at this stage that some side-reactions or impurities present in the system may produce other highly coloured ions. For example, a sample of the styrene dimer which, we believe, contained some impurities, on reaction with potassium produced a coloured solution, the spectrum of which showed a strong absorption band at 460 mμ in addition to the expected band 535 mμ. No attempt was made to identify this new species.

It was suggested by Dr. A. Vrancken from this laboratory that the reaction of alkali metals with polystyrenes possessing C=C double bonds in their chains may be profitably used to detect, or even to determine quantitatively, such groupings in the polymer.

DISCUSSION

The results reported show that the spontaneous changes which take place slowly in a solution of " living " polystyrene are caused by two consecutive reactions:

$$\sim\!\!\sim CH_2{\cdot}CHPh^-Na^+ \longrightarrow \sim\!\!\sim CH{=}CHPh + NaH \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$CH_2{\cdot}CHPh^-Na^+ + CHPh{:}CH{\cdot}CHPh{\cdot}CH_2\sim\!\!\sim \longrightarrow \sim\!\!\sim CH_2{\cdot}CH_2Ph + Na^+\ CHPh{:}CH{\cdot}\bar{C}Ph{\cdot}CH_2\sim\!\!\sim \quad . \quad (2)$$

the second reaction following rapidly the slow rate-determining reaction (1). The formation of 1,3-diphenylallyl ions causes the observed spectral changes, and their stability accounts for the inability of the resulting polymers to sustain further growth of the chain.

The first reaction requires dissociation of the ion-pair and migration of the Na^+ ion towards the β-hydrogen. This accounts for the fact that the process is rapid in ether solvents (dimethoxyethane or tetrahydrofuran) (since these facilitate the dissociation) but very slow in benzene. Moreover, it explains the increase of the rate on dilution.

Quantitative observations show that the process is accelerated by the contact of the

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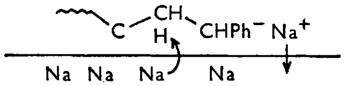
[7] Tiers, *J. Chem. Phys.*, 1951, **19**, 1072.

solution with alkali metal. We suggest that on the surface of the metal a process of the following type might catalyse the reaction:



The presence of two negatively charged ends in our polymers is responsible for the observations mentioned earlier, *e.g.*, the dependence of the rate of the process on the molecular weight of the polymer. Such effects, originating from the repulsion between the charged ends, are observed in other studies, *e.g.*, of the equilibria [8] between monomer and polymer and of the dependence of propagation rate constant [9] of the reaction $\mathrm{P}^*_n + \mathrm{M} \rightleftharpoons \mathrm{P}^*_{n+1}$ on the degree of polymerization.

The process described here may be followed by further and even slower reactions, *e.g.*,

$$\mathrm{Na^+ + {\sim\sim}CH_2{\cdot}\bar{C}Ph{\cdot}CH{:}CHPh \longrightarrow {\sim\sim}CH{:}CPh{\cdot}CH{:}CHPh + NaH}$$

and this in turn may produce the diphenylbutadiene radical-ion (in the presence of alkali metal), or the pentadienyl anion (in the presence of " living " polymers). Whatever is the nature of the side reactions which accompany the main decomposition, it appears that some of them produce free spins which are recognizable by their electron-spin resonance signal. In our studies no such signal has been observed in a solution of non-isomerized, " living " polystyrene of high molecular weight. However, a solution of non-isomerized " living " polystyrene of low molecular weight (DP 2—5) gave a weak signal which we could not resolve. This signal is due probably to styrene monoradical-ions which are in equilibrium with the respective dimeric di-ions,

$$\mathrm{{}^-Ph{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHPh^- \rightleftharpoons 2[{\cdot}CH{-}CHPh^-]}$$

On the other hand, as " living " polystyrene is transformed into the allyl ion a strong signal appears, showing a complex hyperfine structure containing more than 80 lines. A signal resolved into 23 main lines has also been observed from a solution formed on reaction of potassium with 1,3-diphenylbut-1-ene. A detailed account of all these spectra will be published later.

A comprehensive study of electron-spin resonance spectra observed in the " living " polystyrene system has been recently reported by Morigagi *et al.*[10] However, the solutions investigated by these workers were heated for a prolonged time to 100° before examination. This treatment undoubtedly destroys the original material and hence it is difficult to say what species produced the spectrum. Obviously, the conclusions drawn by Morigagi *et al.* are disputable and probably not pertinent to the mechanism of anionic polymerization.

The reaction of " living " polystyrene with alkali metal results in two processes. As the " living " polymer is in equilibrium with its monomer, the solution must contain free styrene. The latter reacts with alkali metal by an electron transfer, forming the negative styrene radical-ion which mainly dimerizes (since the low concentration of styrene does not favour the polymerization). The net effect of this reaction is two-fold: the concentration of alkali in the solution increases and the degree of polymerization decreases.

One might expect that the depropagation may be the rate-determining step, particularly if stirring is very vigorous. Unfortunately, this is not the case. The initial rapid uptake of alkali is soon slowed down since the $\sim\mathrm{CH_2{\cdot}CHPh^-}$ end groups are changed into $\sim\mathrm{CH_2{\cdot}CPh^-{\cdot}CH{=}CHPh}$ end groups, and probably the latter are only slowly dissociated in a heterogeneous reaction involving the alkali metal. Thus, under these conditions, degradation of the polymer to the dimer never goes to completion since a large fraction of the " living " ends is terminated by proton transfer.

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[8] Vrancken, Smid, and Szwarc, *J. Amer. Chem. Soc.*, 1961, **83**, 2772.

[9] Unpublished results from this Laboratory.

[10] Morigagi, Kuwata, and Hirota, *Bull. Chem. Soc. Japan*, 1960, **33**, 952, 958.

The decomposition of dimers may produce such compounds as 1,4-diphenylbutadiene di-anion and its monoradical ion, *i.e.*:

$$\mathrm{Na^+,{}^-CHPh{\cdot}CH_2{\cdot}CH_2{\cdot}CHPh^-Na^+} \longrightarrow \mathrm{CHPh{=}CH{\cdot}CH_2{\cdot}CHPh^-Na^+ + NaH}$$

$$\mathrm{CHPh{=}CH{\cdot}CH_2{\cdot}CHPh^-Na^+} \xrightarrow{\mathrm{Na}} \mathrm{CHPh{=}CH{\cdot}CH{=}CHPh^{2-}2Na^+ + NaH}$$

Although the presence of these compounds has not been established unequivocally, the spectrum of such a solution is not inconsistent with this assumption. The monoradical-ions formed in this process may also contribute to the electron-spin resonance signal observed in those solutions.

Spectroscopic studies of " living " polystyrene have been recently reported by Kuwata.[11] The electronic spectra presented in his paper show that he was investigating the " isomerized " polystyrene. This is not surprising since his samples were heated for a prolonged time at 100° in contact with an alkali metal. In view of our findings many of his conclusions, albeit not facts, are erroneous.

EXPERIMENTAL

The work described here was carried out on a high-vacuum line in all-glass equipment with break-seals and constrictions instead of stopcocks. This technique, used in all the work in this laboratory, has been described in several Ph.D. theses (*e.g.*, R. Waack, Thesis, Syracuse, 1959). The monomers and solvent were carefully purified (see the above thesis).

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[11] Kuwata, *Bull. Chem. Soc. Japan*, 1960, **33**, 1091.