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Anionic Polymerization of Butadiene in Tetrahydrofuran. I. Isomerization of Polybutadienyl Salts

A. Garton and S. Bywater*

Chemistry Division, National Research Council of Canada, Ottawa, Canada K1A OR9.

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ABSTRACT: The near-uv absorption spectra of polybutadienyllithium, -sodium, and -potassium have been investigated at various temperatures in tetrahydrofuran. It was observed that these changed with temperature and also could depend on the presence or absence of a polymerization reaction. These changes are correlated with differing cis and trans populations of the active center. With the lithium and sodium compounds the cis content at equilibrium increases with decreasing temperature. The monomer addition step favors the formation of trans active centers, and at low temperatures the cis–trans population deviates markedly from equilibrium. Polybutadienylpotassium shows more complex behavior. An irreversible isomerization to another form of the active center masks the simple cis–trans isomerization.

Early studies of the electronic spectra of anionic polymerization systems particularly in polar solvents have shown that the growing active centers are not always stable. Besides attack on the solvent leading to a decrease in their concentration, so-called isomerization reactions can occur, often leading to new species which are inactive in further homopolymerization. Such is the case with polystyrylsodium in tetrahydrofuran[1,2] (THF), although this fortunately is a relatively slow reaction. Anions of the diene monomers are even less stable in this solvent at room temperature[3,4] although stability is better at lower temperatures.[5] Some of the dienyl anions, e.g., polyisoprenyllithium can re-form the original anions after isomerization by the addition of further monomer. Recent studies of oligomeric polyisoprenyl- and polybutadienyllithium have indicated that both cis and trans forms of the active ends exist in solution,[6–8] the cis form predominating in the former case at all temperatures in tetrahydrofuran. Polybutadienyllithium on the other hand at equilibrium is a mixture of the two at 0°, the cis form being favored at low temperatures. It is clear that a number of processes leading to a change in the nature of the active species can occur. All of these have been previously described as "isomerizations" although strictly speaking some are chemical reactions (e.g., polystyrylsodium[2]) and are irreversible. Some suggested changes can be more properly described as rearrangements (e.g., polyisoprenyllithium[4]) but in addition with the dienes reversible geometrical isomerization can occur. The absorption spectra of polydienyl anions under polymerization conditions are normally found to be rather broad compared with the absorption bands found for polystyryl compounds which suggests that more than one species exists in solution. Although studies of the kinetics of diene polymerization in THF have been made, it is clear that interpretation of the results is very difficult unless one knows to what species the observed rates apply. A study has been made, therefore, of the spectra of polybutadienyllithium, -sodium, and -potassium in THF as a function of reaction conditions in an attempt to elucidate some of the changes taking place.

Experimental Section

Butadiene (Phillips Research Grade) was degassed under vacuum before being condensed onto butyllithium. It was allowed to polymerize for 40 min at −10°. This procedure was repeated once more before storage in the gas phase in blackened 5-l. bulbs. The purifications of THF and styrene have been described previously.[9] Sodium tetraphenylboride (Fisher Scientific) was purified as described by Parry et al.[10] The lithium salt was prepared in the same way. Potassium triphenylcyanoboride, used because of the low solubility of the tetraphenylboride salt, was precipitated from a concentrated aqueous solution of the commercially available sodium salt (K&K Laboratories) by the addition of an equivalent amount of concentrated aqueous reagent grade potassium chloride, and subsequently recrystallized from ether–cyclohexane. The sodium content was found to be less than 0.7%.

The experimental procedures, involving breakseal techniques and greaseless high-vacuum systems, have been reported in earlier communications from these laboratories. Initiation of polymerization was attained either by contacting butadiene with the appropriate alkali-metal film or by use of the corresponding oligomeric polystyryl salt prepared in benzene and subsequently freeze dried to remove the solvent. In the former case, the solvent originally distilled into the reaction vessel from Na/K alloy was finally dried over an alkali-metal film *in situ*. This procedure was found to be

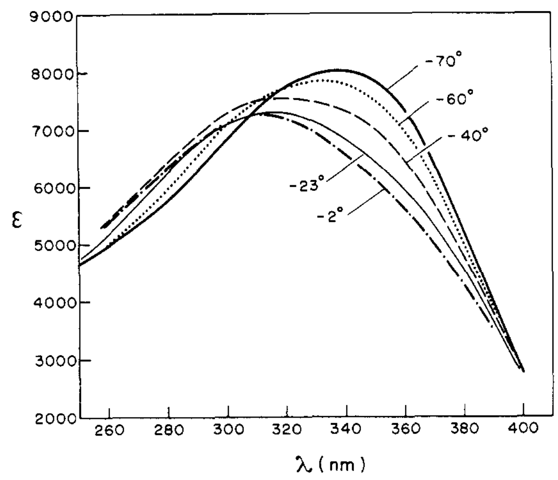

Figure 1. Uv absorption spectra of polybutadienylsodium observed during polymerization at various temperatures. (Sodium tetraphenylboride present.)

preferable to use of alkali-metal salts of α-methylstyrene or 1,1-diphenylethylene. With the α-methylstyrene technique, residual traces of it were difficult to remove and caused changes in spectra once all the butadiene was consumed. 1,1-Diphenylethylene, despite purification over a sodium mirror, still showed evidence for the presence of an impurity, probably biphenyl, which produced anomalies in the observed spectra. With polystyryl salt initiation an extra bulb of this salt was used to wash the inside of the apparatus followed by refluxing solvent from the solution. Butadiene was introduced from a small flask sealed to the reaction vessel via a breakseal. All other reagents were added in fragile bulbs crushed as required by a magnetic breaker.

Initiation and mixing of the reactants was performed rapidly in a large stainless steel dewar vessel containing methanol maintained roughly at the same temperature as required in that particular experiment. Electronic spectra were measured in a Cary-14 spectrophotometer equipped with a quartz dewar vessel with optically clear windows.[11] The temperature inside was maintained at the required value by circulation of methanol from a Lauda thermostat bath capable of maintaining temperatures down to −75° with a precision of ±0.1°. The observed spectra were not dependent on the mode of initiation with one exception noted later. The extinction coefficients of polybutadienyl anions were determined from those of the precursor polystyryl salts. For this purpose, the extinction coefficient of polystyryllithium at 336 nm was assumed to be 1.30×10^4 l. mol^{-1} cm^{-1} at 22°. Measurements of its spectrum at a number of lower temperatures established that the extinction coefficient at 336 nm (ϵ_{max}) increased by 0.11% per degree as the temperature decreased after allowance for concentration changes on cooling. Polystyrylsodium and -potassium were assumed to have identical extinction coefficients to that of the lithium salt. The concentration of added tetraphenylboride salt was also measured spectrophotometrically. The extinction coefficient of sodium tetraphenylboride at 273 nm and 25° was found to be 2220 l. mol^{-1} cm^{-1} in agreement with Bhattacharyya et al.[12] Lithium and potassium salts were assumed to have this extinction coefficient also.

Results

The spectra of the active centers normally observed in polymerizing polybutadienylsodium in tetrahydrofuran at various temperatures are shown in Figure 1. The reaction conditions, suitable for the study of ion pair propagation rates, were [butadiene] ~0.2 *M*, [active centers] $\sim 10^{-3}$ *M*, [sodium tetraphenylboride] $\sim 10^{-3}$ *M*. At a given temperature, insignificant changes were observed with time during the first three half-lifetimes of polymerization except at −70° where initial and final spectra showed some differences. It is clear, however, that the nature of the active species changes with polymerization temperature. The differences at very low temperature suggested a more careful examination of the time dependence of the spectra. It was found that if the initial monomer concentration was lower (~0.03 *M*) and particularly if no sodium tetraphenylboride was added, sharper spectra with maxima displaced to shorter wavelengths were observed after a few minutes. In the absence of added salt, polymerization is very rapid with sodium as counterion (half-lifetimes of less than 1 min at −40 or −70°). If to this system the normal amount of monomer (~0.2 *M*) was subsequently added the spectrum rapidly broadened and shifted to longer wavelength giving a spectrum almost identical with that observed under normal polymerizing conditions. The spectrum then slowly reverted to its original form. An example is shown in Figure 2.

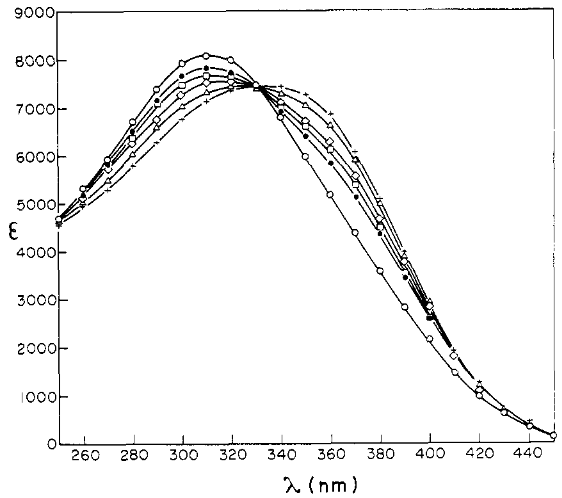

Figure 2. Spectra of polybutadienylsodium at −40°. (○) Initial spectrum produced by adding a small amount of monomer and allowing to equilibrate. (+) 3, (△) 9, (◇) 14, (□) 20, and (●) 41 min after the subsequent addition of 0.2 *M* butadiene. (No sodium tetraphenylboride added.)

Broadening of the sharp spectra produced at −40° could also be achieved by warming the solution to 0° even without the addition of more monomer. The spectrum was then closely similar to that produced during polymerization at this temperature. It was found necessary in this case to add sodium tetraphenylboride at −40° before warming to 0° for reaction with the solvent is quite rapid at the higher temperature. The small proportion of free anions present in the absence of an ionization suppressant appear to be very reactive toward solvent. The ion pair however only reacts very slowly with solvent at 0°. In summary these results show that at 0° the spectrum observed is independent of the presence or absence of polymerization but at lower temperatures marked differences occur.

Similar effects are observed with lithium as counterion. The ion pair rates are very much lower in this case and were not determinable below −10°. All spectral investigations were therefore carried out in the absence of tetraphenylboride. Even under these conditions the half-lifetime for polymerization was nearly 1 hr at −40°. In this case the effect of addition of 0.2 *M* monomer to a nonpolymerizing system was investigated at three different temperatures. At −12° the differences between polymerizing and nonpolymerizing systems were small. At −40° the results were similar to those shown in Figure 2. At −70°, however, the spectrum broadened and shifted to longer wavelength on the addition of the second and larger batch of monomer, but failed to return to its original form in measurable times. The rate of exchange between the different types of active center is extremely low at this temperature. Under these conditions it is not certain that the initial sharp spectrum produced accurately represents species

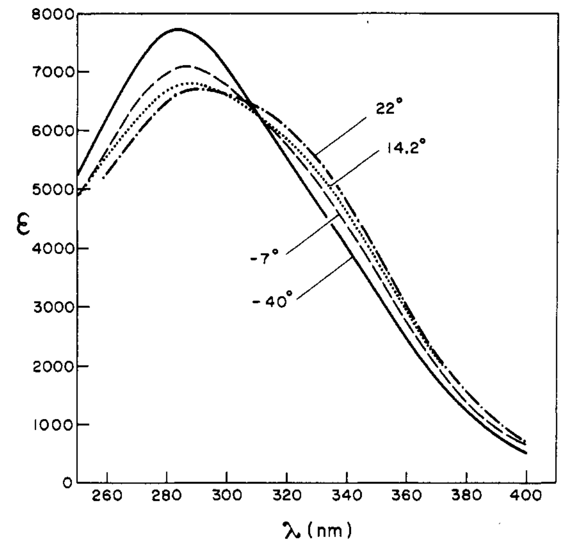

Figure 3. Spectra of polybutadienyllithium at equilibrium at various temperatures.

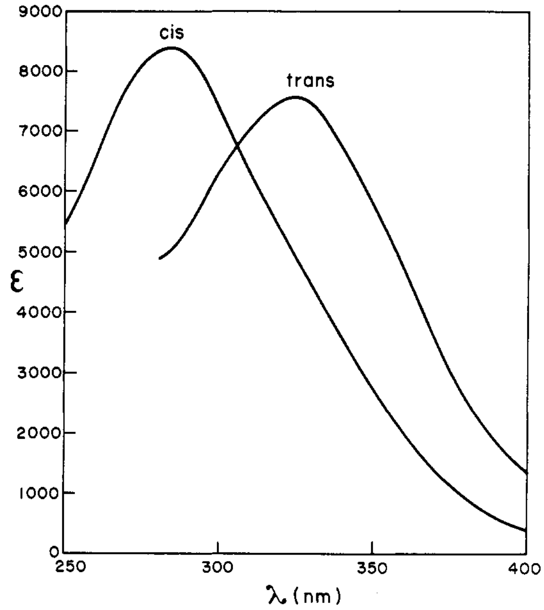

Figure 4. Estimated spectra of the cis and trans forms of the active center of polybutadienyllithium at −40°.

completely at equilibrium. Nevertheless with this restriction in mind, a series of curves can be constructed which should closely represent the spectra corresponding to species stable at a series of temperatures. These broaden and move to longer wavelength as the temperature is increased (Figure 3). A comparison of selected curves in Figures 1 and 2 shows the same effect occurs in the sodium-based systems. (Compare the 0° curve in Figure 1 characteristic of all systems at this temperature and the sharp spectrum at −40° in Figure 2.) On the other hand, under conditions of rapid polymerization, the reverse trends occur as the temperature is increased (Figure 1).

Attempts to facilitate the production of sharp spectra by reducing the initial amount of butadiene added to 3–4 molecules per active center did not meet with success. Anomalous spectra were obtained using polystyrylsodium or -lithium initiation. The extinction coefficients were higher than expected and spectra possessed a very long wavelength tail. At −40° these spectra did not pass through the isobestic point shown in Figure 1. When more butadiene was added the spectra reverted to the standard type. It appears that the spectra of anions having only a few butadiene units are abnormal, or else that there are side reactions in the addition of butadiene to polystyryl salts. It is interesting in this regard to note that we were unable at any time to reproduce the spectrum of polybutadienylsodium at −40° reported by Gourdenne[5] which has a very sharp maximum at 293 nm. From the description of the experimental procedure used it seems that this product also, initiated on a sodium mirror, could have a very short chain length. On the other hand the reported maximum at 310 nm in systems involving more added monomer, used in block polymer formation, is in reasonable agreement with the present results.

With potassium as counterion, the results are less clear. At −40° relatively sharp spectra with a maximum at 320 nm can be obtained by the techniques described above. On warming to 0°, unlike the situation observed with the other counterions, little change was observed. Both at 0° and −40° quite broad spectra were observed during polymerization. At the higher temperature, there was a tendency to return to the sharper form on completion of polymerization but this was rapidly followed by extensive broadening to give a marked shoulder at 380–385 nm. It appears that an irreversible isomerization is superposed on the simple reversible process. Much the same long wavelength absorption can be observed with polybutadienylsodium at room temperature, but it only becomes evident after most of the polymer anions have been destroyed by reaction with solvent.

Discussion

The variations in spectra reported indicate that the active end of polybutadienyllithium and -sodium can exist in more than one form. The different forms are interconvertible with certain limitations. It is reasonable to assume that two major species exist, namely cis and trans forms by comparison with the NMR data produced earlier on oligomers of polybutadienyllithium of dp = 6.[8] In that work, the cis content was found to be 66% at 0°, rising to 83% at −40°. These figures should correspond to equilibrium populations as the monomer–initiator ratio was low and ample time was available for equilibration. The NMR results are also in agreement with a sharpening of the electronic spectrum observed in the present work as the temperature is lowered corresponding to the predominance of the cis form at low temperatures (Figure 3). On this basis, the cis form would have a maximum in its spectrum at 285 nm and the trans form a maximum at 325 nm. In fact the individual curves can be reconstructed assuming the isomer ratio is the same in both sets of experiments although obtained under widely different concentration ranges (Figure 4). The accuracy is somewhat limited because the isomer ratio does not change drastically in 50° and in addition no correction can be made for natural line sharpening which occurs as the temperature is decreased in all such spectra. The apparent difference in extinction coefficients may therefore not be real.

By analogy it can be suggested that with the sodium compound the cis maximum is at 310 nm and the trans maximum is at 350 nm and that the cis form is more stable at low temperatures. The situation is less clear for polybutadienylpotassium. No evidence was found for changes in the equilibrium population of the cis and trans isomers with changing temperature. When polymerization is proceeding very broad spectra are always obtained with large optical densities in the 380–400-nm region. In this case there must be a suspicion that at all except the very lowest temperatures more complex and irreversible isomerization reactions cannot be avoided.

If consideration is restricted to the lithium and sodium compounds, at equilibrium the concentration of cis active centers increases at lower temperatures, but the spectra indicate that during polymerization the trans form becomes increasingly predominant as the temperature is lowered (Figure 1). It appears that monomer addition preferentially forms a new growing center of the trans form. At 0°, the observed spectra are independent of the presence or absence of a polymerization reaction. There the active end must have ample time to reorganize to its stable form (a mixture at this temperature) between successive monomer addition steps. As the temperature is lowered, increasing divergence is shown between equilibrium and polymerization states. At −40°, despite this fact, during a polymerization in the presence of sodium tetraphenylboride (Na^+ counterion) no change in spectrum is observed over 90% of the polymerization process. It must be supposed that cis → trans and trans → cis changes induced by monomer addition are in balance to give a higher than normal trans population. The lifetime of an active center is at most 1.5 min between successive additions of monomer which is insufficient to allow the system to revert to a high cis concentration. The time scale for natural isomerization at this temperature (Figure 2) is much larger. At −70° there is some increase in trans content of the active centers at least in the early stages of polymerization which suggests that cis → trans changes have become slower. Similar observations were made using lithium as counterion although in the absence of lithium tetraphenylboride in order to produce measureable polymerization rates. The presence of variable amounts of cis and trans active centers must have important implications in studies of reaction kinetics. These are considered in part II.

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Anionic Polymerization of Butadiene in Tetrahydrofuran. II. Ion Pair Propagation Rates

A. Garton and S. Bywater*

Chemistry Division, National Research Council, Ottawa, Canada, K1A 0R9.

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ABSTRACT: The ion pair propagation rates for polybutadienyllithium, -sodium and -potassium have been measured in tetrahydrofuran. Rates were lowest with lithium as counterion and could only be measured down to −10°. The sodium rates were higher but showed a decreasing apparent activation energy at lower temperatures. These results are correlated with changes in the cis–trans ratio of the active center with temperature. The highest rates were observed with potassium as counterion but in this case even at −40° it is suspected some irreversible isomerization may have occurred.

Much information is available on the propagation constants attributed to the various types of active center in the anionic polymerization of styrene in cyclic ether solvents. The contributions to the overall reactivity of free ions and both contact and solvent separated ion pairs have received extensive study.[1] Less is known about the propagation process with other monomers and indeed few of them provide the absence of side reactions necessary for a detailed kinetic investigation. The dienes seem to be suitable candidates for further study although their polymerization is more susceptible to side reactions than is styrene, at least at room temperature. Stability of the active centers is better at lower temperatures. In part I, the nature of the isomerization reactions in the anionic polymerization of butadiene was examined in tetrahydrofuran. It was found that attack on the solvent was not too important below 10° if ionization of the active centers was suppressed, and that at least with lithium and sodium counterions no irreversible isomerization occurred. Cis and trans forms of the active centers could however be recognized.

Early kinetic studies of anionic polymerization in THF[3,4] were carried out in the absence of ionization suppressing salts and the rates measured include both ion and ion pair contributions to the propagation rate. More recently the sodium–butadiene–THF system was studied at low temperature in the presence of sufficient sodium tetraphenylboride so that true ion pair propagation constants could be evaluated.[5] Also while this work was in progress, the ion pair propagation constants for the potassium-based system were determined in the temperature range 0 to −13°.[6] In order to correlate the kinetic study of the system with the spectral changes observed earlier it was thought worthwhile to reexamine the rate data.

Experimental Section

Details of the experimental procedures followed have been described in part I. The rate of consumption of butadiene was followed spectrophotometrically at about 245 nm where the absorption of the anions is low. Typical reaction conditions involved an active center concentration of about 10^{-3} *M* and an initial monomer concentration of about 0.2 *M*. Ionization was suppressed by the addition of $>10^{-3}$ *M* tetraphenylboride salt (cyanotriphenylboride in the case of potassium). The concentration of the active