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.

References and Notes

(1) M. Levy, M. Szwarc, S. Bywater, and D. J. Worsfold, *Polymer*, **1**, 515 (1960).
(2) G. Spach, M. Levy, and M. Szwarc, *J. Chem. Soc.*, 355 (1962).
(3) S. Bywater, A. F. Johnson, and D. J. Worsfold, *Can. J. Chem.* **42**, 1255 (1964).
(4) S. S. Medvedev and A. R. Gantmakher, *J. Polym. Sci., Part C*, **4**, 173 (1963).
(5) A. Gourdenne and P. Sigwalt, *Eur. Polym. J.*, **3**, 481 (1967).
(6) F. Schué, D. J. Worsfold, and S. Bywater, *Macromolecules*, **3**, 509 (1970).
(7) W. H. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, *J. Organomet. Chem.*, **51**, 13 (1973).
(8) S. Bywater, D. J. Worsfold, and G. Hollingworth, *Macromolecules*, **5**, 389 (1972).
(9) S. Bywater and D. J. Worsfold, *J Phys. Chem.*, **70**, 162 (1966).
(10) A. Parry, J. E. L. Roovers, and S. Bywater, *Macromolecules*, **3**, 355 (1970).
(11) G. Löhr and S. Bywater, *Can. J. Chem.*, **48**, 2031 (1970).
(12) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **88**, 307 (1966).

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

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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

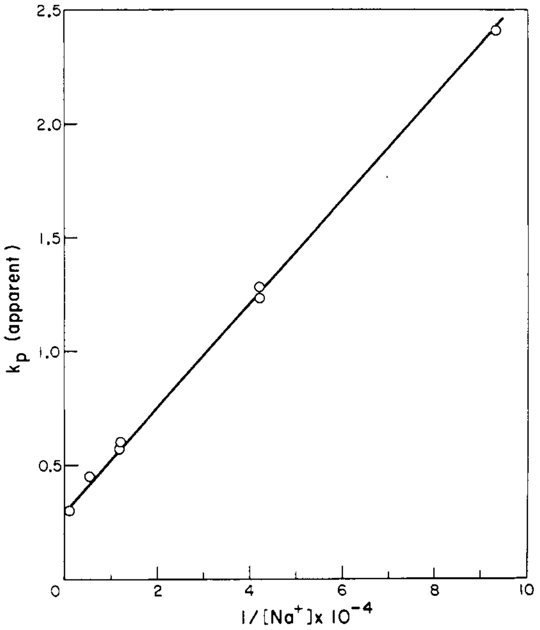

Figure 1. Apparent k_p (l. mol^{-1} sec^{-1}) for polybutadienylsodium at −70° as a function of reciprocal sodium ion concentration.

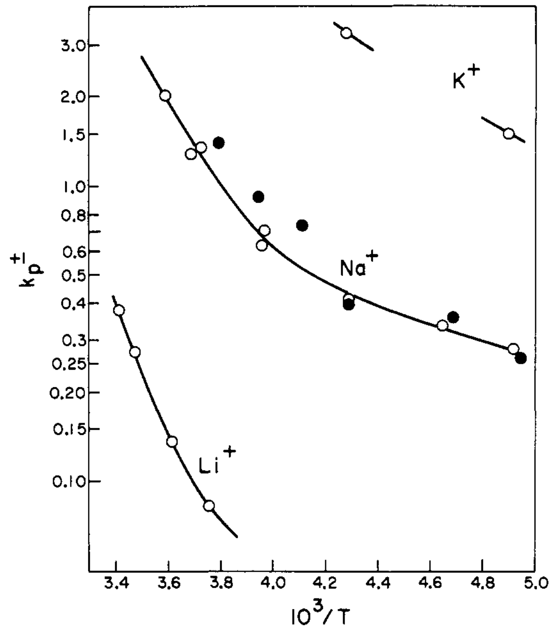

Figure 2. Variation of ion pair propagation constants (l. mol^{-1} sec^{-1}) with temperature and counterion: (○) present results; (●) averaged values from ref 5 (Na^+).

centers was normally determined from the concentration of the polystyryl salt used as initiator. The extinction coefficients assumed for this compound were described in part I. In a few experiments initiation was produced by contacting the butadiene with the appropriate alkali metal film. In this case the active center concentration was determined from the absorption band of the polybutadienyl anion. The extinction coefficient used was based on experiments at the same temperature involving polystyryl salts. Care is necessary if this procedure is used because of the variations in absorption spectra caused by cis–trans isomerization. Suitable isobestic points are available. The total sodium ion concentration required for some experiments was determined from the dissociation constant of sodium tetraphenylboride,[7] the contribution from the dissociation of the polybutadienyl anion pair being negligible under our experimental conditions.

The reaction was followed in most cases to about three half-lifetimes of the butadiene monomer. Either Guggenheim plots[8] were used to determine the first-order constant of monomer decay or simple logarithmic plots of monomer concentration if a final optical density could be estimated (often both methods were used). When working at very low temperatures some drift of the coolant blank in the quartz dewar was observed possibly due to condensation. The necessary correction to the observed rate was small, but long-term stability problems in the optical system do limit the accuracy and place a lower limit on the rate constants which can be determined with accuracy.

The microstructure of the polymer produced was determined by ^1H and ^{13}C nuclear magnetic resonance spectroscopy using Varian HA-100 and CFT-20 instruments. Solutions in $CDCl_3$ (15%) were used at room temperature. Polymer molecular weights were of the order of 50000.

Results

In order to determine the amount of tetraphenylboride salt required to suppress ionization, initial experiments with Na^+ as counterion were carried out at −70° at various concentrations of added salt. The results are shown in Figure 1 where k_p (apparent) (i.e., the first-order constant divided by active center concentration) is plotted against reciprocal $[Na^+]$ as suggested by Bhattacharyya et al.[9] The intercept gives the ion pair propagation constant ($k_p^{\pm}$) and the slope, the $k_p^-K_D$ product, where k_p^- is the free anion propagation constant and K_D the ion pair dissociation constant. A sodium ion concentration of $\sim 10^{-3}$ *M* equivalent to a sodium tetraphenylboride concentration of $\sim 2 \times 10^{-3}$ *M* is required to give a k_p value within 10% of the true $k_p^{\pm}$ value. The dissociation constant of sodium tetraphenylboride hardly changes with temperature so the presence in the reaction mixture of tetraphenylboride concentrations of this order of magnitude should be adequate at higher temperatures to determine $k_p^{\pm}$ directly. This simple procedure was therefore used at higher temperatures. No attempt was made to determine accurately K_D and k_p^- but the results in Figure 1 together with a single experiment carried out in the absence of sodium tetraphenylboride suggest values of $\sim 10^{-9}$ and $\sim 10^4$, respectively, at −70°. As polymerizations with Li^+ as counterion are considerably slower than with sodium in the absence of added salt, K_D must be considerably lower in this case and lithium tetraphenylboride concentrations $\sim 10^{-3}$ *M* more than adequate to suppress the free anion reaction.

Figure 2 shows the $k_p^{\pm}$ values obtained for polymerizations with the three counterions Li^+, Na^+, and K^+ as a function of reciprocal temperature. The most striking feature observable is the very nonlinear Arrhenius plot obtained with sodium as counterion. The lithium results have, by analogy, been drawn assuming a slight curvature at lower temperatures although a linear plot would fit the results equally well within experimental error. Unfortunately in this case rates below −10° were too slow to measure with any accuracy for the reasons noted above. The assumption mentioned leads to an activation energy 9.8 kcal mol^{-1} at the higher temperatures with a preexponential factor of 10^7. As the points for sodium curve markedly activation energies are difficult to establish but must be >7 kcal mol^{-1} at the higher temperatures decreasing to ~1 kcal mol^{-1} at the lower temperature.

The appearance of a curved Arrhenius plot was noted in the earlier results with sodium as counterion[3] where no added salt was present although the observed rates were naturally higher. The true ion pair constants determined by Funt[5] for polybutadienylsodium are close to those determined here being on average about 40% higher which is perhaps not surprising considering the quite different experimental methods used. These authors considered that their results at 2×10^{-2} *M* added tetraphenylboride salt could be reasonably fitted to a line of constant activation energy of 2.6 kcal mol^{-1}. They did however note that at a lower salt concentration (3.6 × 10^{-3} *M*) a definite curve was obtained. The lower concentration of salt is amply sufficient to suppress the free anion reaction and it appears to us that their results even at the highest salt concentration can equally well be fitted by a curved line also.

Only a limited study of the polymerization was made with potassium as counterion because of doubts about the presence of irreversible isomerization products. The spectra of the active centers were rather broad although at least at −70° no marked shoulder at 380 nm was apparent. At −40° however a marked shoulder was apparent at this wavelength at the end of reaction. The two rate constants measured at −40 and −70° are higher than those determined by Fontanille[6] in the temperature range 0 to −10°. A similar phenomenon has been observed with polyisoprenylsodium in THF which we attribute to increasing amounts of irreversible isomerization to a less reactive species as the temperature is raised.

Discussion

The appearance of a variable apparent activation energy for polybutadienylsodium is not surprising considering the evidence presented in part I that the nature of the active species changes with changing temperature. Similar changes occur with polybutadienyllithium but unfortunately the kinetic measurements could not be extended to the lower temperature range where the changes are most marked. At about 0° the spectrum of polybutadienylsodium is independent of the presence or absence of a polymerization reaction (Figure 3). The observed spectra appear to correspond to an equilibrium mixture of cis and trans forms. At lower temperatures, the spectra are shifted increasingly to longer wavelength during polymerization. This was suggested (part I) to be caused by increasing amounts of the trans form in solution. Correspondingly in the kinetic measurements, the apparent activation energy drops sharply. It seems that not only is the trans form of the active center the kinetically preferred product but that at least at low temperatures it also has a higher reactivity toward monomer than has the cis form. The net result particularly between −40 and −70° would be an increasing population under polymerization conditions of a more reactive species producing a slowing of the normal decrease in reaction rate as the temperature is decreased. Determination of the dominant process at higher temperatures is not possible because the active ends appear to equilibrate quite rapidly. It must be presumed that some of the alternative processes perhaps of higher activation energy become important at these temperatures.

Similar decreases in apparent activation energy as the temperature is lowered have been observed with styrene polymerization (counterion Na$^+$) in tetrahydropyran[10] and oxepane.[11] They were attributed to an increasing fraction of more reactive solvent-separated pairs at lower temperatures. Changes in uv absorption spectra of fluorenylsodium with temperature in tetrahydrofuran have been described[12] caused by the same effect. Although there are some superficial similarities with the present system, the presence of solvent-separated pairs at low temperatures is not likely to be the cause of the spectral and rate changes observed with butadiene. The interconversion rate between species of different absorption spectrum is far too low for the change between contact and separated pairs and the differences between polymerizing and nonpolymerizing systems cannot be accounted for in this manner. In addition, the order of reactivity with monomer falls in the series K$^+$ > Na$^+$ > Li$^+$ as counterion is varied. As the Li$^+$ ion is known to be the most susceptible to solvent-separated pair formation, propagation rates should be higher with this counterion if separated pair formation were important. A lower activation energy and a more marked curvature of the Arrhenius plot at higher temperatures would also be expected. The variation of rate constant with counterion is somewhat larger than observed with polystyrylsodium in dioxane[13] where the presence of contact pairs gives the same order of reactivity as observed in the present investigation. Exact comparisons are however made difficult by the fact that more than one rate constant for monomer addition exists for butadiene. The equilibrium population of cis and trans active centers does not seem to be markedly different between Li$^+$ and Na$^+$ as counterions, but some differences in apparent rate constant could be produced from population differences.

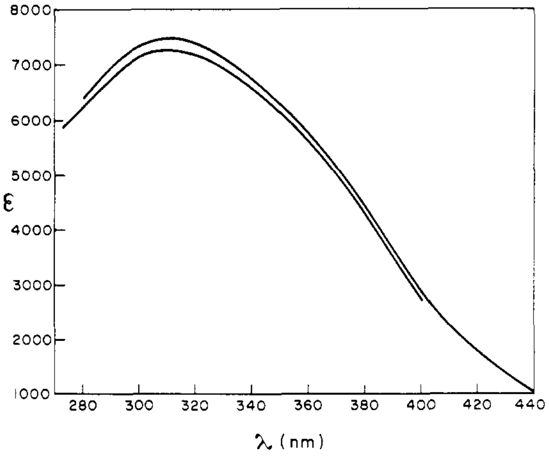

Figure 3. Polybutadienylsodium spectra at −1 to −2°. Upper curve, equilibrium spectrum. Lower curve, observed during a typical polymerization.

The presence of geometrical isomers of the active center could have some influence on the microstructure of the polymer formed. No direct relationship would be expected since most of the units incorporated into the chain are 1,2 in structure whereas the active center itself is basically 1,4 in character.[14] Appreciable delocalization of charge to the γ position as observed in THF seems to favor monomer attack at this position leading to a 1,2 unit in the polymer. Nevertheless, some 1,4 units do exist in the chain and if these are formed by retention of the configuration of the active center when monomer adds at the α position, some changes might be expected as the reaction temperature is altered. Table I gives the polymer microstructure observed at 0 and −70°. Analysis of the ^{13}C spectra was made using the assignments of Alaki et al.[15] and the bands at δ (TMS) 25.1 and 30.3 ppm attributed to cis-vinyl and trans-vinyl pairs. The 1,4–1,2 ratio was determined from ^{1}H spectra. Cis-1,4 units comprise nearly 30% of the total 1,4 content at 0° but are barely detectable at −70°. The major effect, however, of lowering the polymerization temperature is an increase of 1,2 content at the expense of the cis units. The

Table I
NMR Analysis of the Microstructure of Polybutadiene Formed by the Ion Pair Propagation Process in THF[a]

Sample	Polymerization temp, °C	Cis, %	Trans, %	1,2, %
P1	−70	≤1	13	86
P2	0	6	14	80

[a] Counterion Na$^+$.

trans content remains largely unchanged. As nothing is known of the relative tendencies of cis and trans active centers to form 1,2 or 1,4 in-chain units or how this varies with temperature, perhaps the only significant observation is the virtual disappearance of cis units in the chain.

References and Notes

(1) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes", Interscience, New York, N.Y., 1968, Chapter 7.
(2) A Garton and S. Bywater, *Macromolecules*, **8**, preceding paper in this issue (1975).
(3) A. A. Arest-Yakubovich and S. S. Medvedev, *Dokl., Akad. Nauk SSSR*, **159**, 1066 (1964).
(4) M. Morton, E. E. Bostick, R. A. Livigni, and L. J. Fetters, *J. Polym. Sci., Part A-1*, 1735 (1963).
(5) B. L. Funt and V. Hornoff, *J. Polym. Sci., Part A-2*, **9**, 2429 (1971).
(6) A. Siove, P. Sigwalt, and M. Fontanille, *Polymer*, **16**, 605 (1975).
(7) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).
(8) E. Guggenheim, *Philos. Mag.*, **2**, 538 (1926).
(9) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).
(10) L. Böhm, W. K. R. Barnikol, and G. V. Schulz, *Makromol. Chem.*, **110** 222 (1967).
(11) G. Löhr and S. Bywater, *Can. J. Chem.*, **48**, 2031 (1970).
(12) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).
(13) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).
(14) S. Bywater, D. J. Worsfold, and G. Hollingsworth, *Macromolecules*, **5**, 389 (1972).
(15) Y. Alaki, T. Yoshimoto, M. Imanari, and M. Takeuchi, *Kobunshi Kagaku*, **29** 397 (1972); *Rubber Chem. Technol.*, **46**, 350 1973.

Stereochemistry and Polymerization of 1,3-Dioxolane Derivatives. VI. Reactivities of Some Stereoisomers of 2-Alkenyl-4,5-dimethyl-1,3-dioxolanes in the Cationic Polymerization by $BF_3 \cdot Et_2O$

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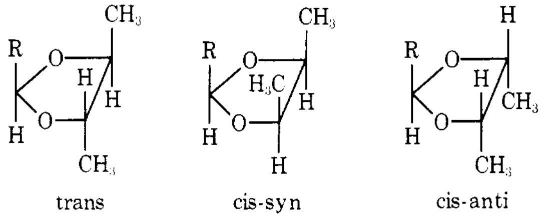
ABSTRACT: The structure–polymerization relationship for some 1,3-dioxolane derivatives was investigated. Trans and cis(syn–anti) isomers of three 2-alkenyl-4,5-dimethyl-1,3-dioxolanes were obtained and then polymerized by BF_3Et_2O in an adiabatic reactor. Polymerization rates R_p were measured. The overall rate of polymerization was found to depend on monomer configuration. For all monomers used, however, polymerization was found to be a first-order reaction with respect to the catalyst and a half-order one with respect to the monomer.

For a number of years the cationic polymerization of cyclic acetals has been a subject of considerable interest. Most of the papers deal with the polymerization and copolymerization of nonsubstituted 1,3-dioxolane, especially with its mechanism in the presence of various catalysts.[1–6] Few papers, however, have been published so far on the polymerization of dioxolane derivatives.[7–15] The polymerization of substituted acetals is a complex process, particularly in the case of acetals with unsaturated substituents for such monomers displaying a bifunctional behavior.

In the case of cyclic acetals containing more than one substituent in the ring stereochemical factors must be taken into account, because such compounds may occur in the form of different stereoisomers. Usually this problem has been neglected in papers dealing with the polymerization of this kind of monomers.

In the present paper the influence of the configuration of such monomers upon the rate of polymerization was taken into consideration. Some stereoisomers of 1,3-dioxolane derivatives were used as model compounds in these experiments. Three unsaturated acetals, 2-vinyl-4,5-dimethyl-1,3-dioxolane (VDMD), 2-isopropenyl-4,5-dimethyl-1,3-dioxolane (IPDMD), and 2-propenyl-4,5-dimethyl-1,3-dioxolane (PDMD), have been investigated. One can get three stereoisomers (nomenclature from Farines[16]) when synthesizing each of the acetals numbered above.

The synthesis and separation of such stereoisomers were described by us earlier[17,18] and some further information is given in the Experimental Section.



Experimental Section

Materials. Acetals have been obtained by means of Fischer's azeotropic method[19] according to the procedure described in some previous publications of ours[17,18] as a result of the reaction of the reaction of *meso*- and dl-butanediol-2,3 (Suchard) with unsaturated aldehydes, acroleine, methacroleine, or croton aldehyde, in the presence of catalytic amounts of *p*-toluenesulfonic acid. In the reaction of the *dl*-butanediol-2,3 and aldehyde, the trans isomer of the corresponding acetal (fraction I) was obtained, whereas in the case of the meso diol a mixture of cis isomers, viz., cis-anti and cis-syn isomers at a ratio of about 2:3 (fraction II), was formed.

The stereoisomeric monomers were distilled over sodium and stored in phials under nitrogen. Their configuration was determined by means of NMR spectroscopy.

Some properties of the monomers were gathered in Table I. The pK_b values presented in Table I were determined by means of the spectrophotometric method.[20]

Catalyst. Boron trifluoride etherate was distilled over phosphorus pentoxide and dissolved in 1,2-dichloroethane.

Solvent. 1,2-Dichloroethane was purified by refining with sulfuric acid and distillation over phosphorus pentoxide.

Polymerization Procedure. The polymerization was carried out in an atmosphere of dry nitrogen in an adiabatic reactor,