charge at vanadium, as found by Olivê et al.[27]

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Anionic Polymerization of Isoprene in Diethyl Ether

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Received May 22, 1979

ABSTRACT: An investigation has been made of the active centers in the anionic polymerization of isoprene in diethyl ether using model compounds. A preference for the cis configuration has been established, although some trans structure can be detected with lithium as the counterion. In this case, association can be detected at concentrations greater than 10^{-3} M. Polymerization rate measurements were made with lithium and potassium counterions. As is usual in polar solvents, the potassium-based system shows faster rates and a lower activation energy. Microstructures of the polymers formed were determined. Some factors determining polymer microstructure are discussed.

The structure of the anion pairs involved in the anionic polymerization of isoprene has been characterized in hydrocarbon solvents and in tetrahydrofuran (THF), principally using the model compound $(CH_3)_3CCH_2CHC(CH_3)CH_2$·metal. Both cis and trans forms exist,[1,2] the stable form for all alkali metals being cis in THF,[3] whereas with lithium in hydrocarbons the trans form predominates.[4,5] This phenomenon is important in the polymerization process since the reactivities of the two forms can differ, and in addition the preferential formation of one of them in the reaction with monomers can affect kinetic behavior[6] or polymer microstructure.[7] Some years ago, Sinn and co-workers[8] investigated the butyllithium-initiated polymerization of isoprene in diethyl ether, but no characterization of the active centers was made. This paper reports such a study in diethyl ether together with measurements of propagation rates for both lithium and potassium counterions.

Experimental Section

The model compound 2,5,5-trimethylhexenyl-2-lithium (I) was prepared in benzene by addition of *tert*-butyllithium to isoprene[9] or in ether from the mercury compound.[3] A trimer was produced by adding two extra molecules of isoprene to it. The corresponding potassium compound (II) was prepared in ether using diisoprenylmercury and a potassium film. NMR measurements were made on ~10% solutions using either Varian HA-100 or XL-100 instruments. Polymer microstructure determinations were also made on the same instruments using the analysis procedure described by Essel.[10] All experiments on the alkali metal systems were carried out using high-vacuum systems. For kinetic measurements, which involve low initiator concentrations, the interior of the glassware was washed with a polydienyllithium solution followed by rinsing with solvent distilled from it.[11] Diethyl ether was washed with aqueous sodium bisulfite, dilute aqueous NaOH, and dilute aqueous H_2SO_4,[12] dried over $MgSO_4$, and finally distilled over CaH_2. It was stored over Na/K alloy. Isoprene (Phillips Research Grade) was purified as described earlier.[13]

Polymerization studies were carried out by the addition of 0.2 M monomer to low molecular weight polyisoprene salts. Polyisoprenyllithium (DP ~ 50) was prepared in hexane using *sec*-butyllithium. The solution was distributed into fragile bulbs, the hexane being pumped-off before sealing. For the other alkali metals, monomer was left in contact with a mirror of the metal for a short time in diethyl ether to produce oligomeric active polymers. Routine measurements of active center concentrations were made using their absorption band in the near-UV: polyisoprenyllithium $\epsilon_{max} = 7600$, polyisoprenylpotassium $\epsilon_{max} = 7800$. Propagation rates were measured from the decrease in optical density at ~240 nm where isoprene absorbs strongly. Since even the lithium compounds were not stable over the several hours required for complete polymerization but decayed at several percent per hour at room temperature, only initial rates were measured. The potassium derivatives were considerably less stable at this temperature.

Results

Compound I was prepared in hydrocarbon solvent and transferred to ether solution at −70 °C as previously described for THF.[2] Isomerization occurred on warming as determined from ^1H NMR measurements on the γ-proton

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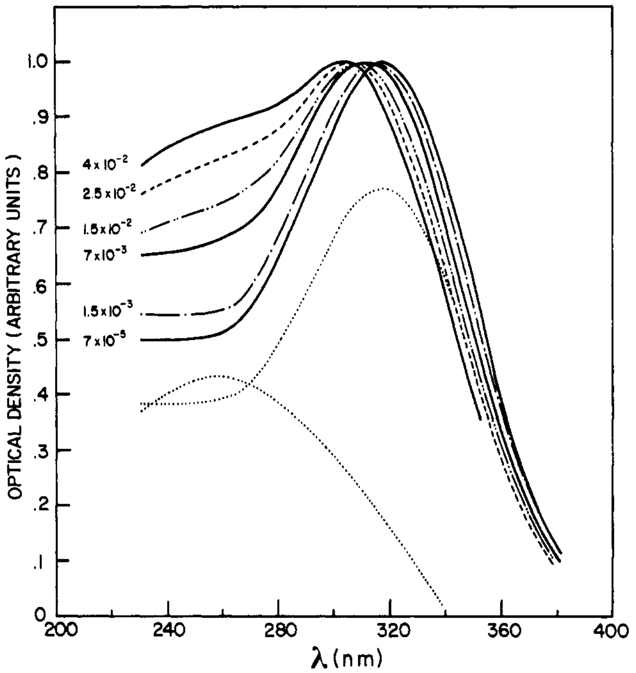

Figure 1. Near-UV absorption spectrum of compound I in diethyl ether at 0 °C. Approximate concentration indicated at left. (···) Individual absorption spectra of monomeric and associated species estimated as described in the text.

resonances (trans δ_{Me_4Si} = 3.80 ppm, cis δ = 3.54 ppm at −10 °C, both slightly dependent on temperature). The cis/trans ratio stabilized at 2.5/1 in the temperature range −20 to +20 °C. Similar results could be observed in ^{13}C NMR experiments. In order to determine if the *tert*-butyl group affects this preference, a trimer was studied by ^{13}C NMR. Signals from the methyl carbon in active centers could be observed at δ_{Me_4Si} = 26.9 ppm (cis) and δ_{Me_4Si} = 20.6 ppm (trans) close to the shifts observed in I. At −20 °C, the cis/trans ratio was within experimental error identical with that of I. ^{13}C NMR measurements on ether solutions of the potassium compound (II) indicated no measurable trans content.

Parallel experiments were made on the near-UV absorption of I. The original ether solutions at −70 °C and $\sim 10^{-2}$ M showed an absorption maximum at 308 nm which moved to 302 nm after warming and recooling. The change from a highly trans to a highly cis structure has a smaller effect on optical absorption than that previously observed in THF.[14] There is however a marked change with concentration. The corresponding figures for λ_{max} are 318 nm (initial) and 316 nm (final) if the experiment is carried out at 10^{-4} M. The UV absorption of I was therefore studied at 0 °C over a wide concentration range (7×10^{-5} to 3.5×10^{-2} M). Little change was observed below 10^{-3} M, but at higher concentration the maximum shifts to shorter wavelength and a shoulder ~260 nm becomes increasingly important (Figure 1). If it is assumed that the symmetrical absorption at 316 nm remains unchanged in shape at higher concentrations, the more complex band under these conditions can be assessed as being caused by two nearly symmetrical bands at 316 and 260 nm. The latter band is probably due to associated species whose active centers are predominantly cis.

The NMR measurements confirm that at high concentrations the predominant species of the lithium compounds is cis. It is possible that in the unassociated form at lower concentrations the cis/trans ratio may be different. It was therefore determined by an alternative procedure, namely the reaction with trimethylsilyl chloride.

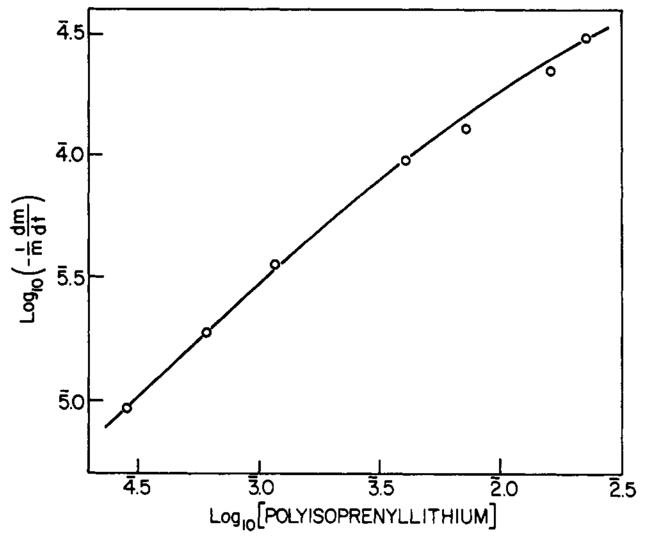

Figure 2. Variation of the first-order monomer reaction rate as a function of poly(isoprenyllithium) concentration (diethyl ether, 18 °C).

The cis and trans forms of the trimethylsilyl derivatives of I can be identified by capillary gas chromatography.[7] By this method over the concentration range 1.5×10^{-3} to 0.4 M, the cis/trans ratio was found to be 2.3 ± 0.1, within limits of error identical with that found by NMR.

In polymerizing systems in diethyl ether (lithium counterion) it is found that the active center absorption also is sensitive to concentration. No changes were found during polymerization. The maximum appears at 323 nm, displaced from that of I, at concentrations $\leq 10^{-3}$ M but moves to shorter wavelengths as concentration is increased (i.e., λ_{max} = 313 nm at 2×10^{-3} M). In a manner similar to that observed with I, there is also a relative increase in absorbance at ~260 nm which we attribute to increasing association with increasing concentration. In parallel, the propagation rate which is close to first order in active centers at $c^* < 3 \times 10^{-3}$ M (Figure 2) becomes less sensitive to concentration above this concentration. This effect has already been suggested[8] to be caused by association to inactive species. The observed k_p in the first-order region is 3.2 M^{-1} s^{-1} at 18 °C, close to that value previously determined at 20 °C.[8] Some error will be caused in the present study because concentrations were determined using ϵ_{max} = 7600 as determined at the high concentrations ($\sim 10^{-2}$ M) required for alkali metal analysis. The extinction coefficient is undoubtedly higher at $c^* < 10^{-3}$ M since the shoulder at 260 nm decreases. The error in concentration determination is however unlikely to be more than 25%. The true k_p could therefore be up to 25% higher than that reported above. At 1.5 °C, the rates were too low for accurate measurement but were in the region of $7–9 \times 10^{-3}$ M^{-1} s^{-1}. The previously reported activation energy (15.8 kcal mol^{-1})[9] is probably too high; values between 12 and 13 kcal mol^{-1} appear more reasonable.

A few polymerization experiments were carried out with sodium as counterion, but only very low concentrations of active centers ($\sim 10^{-5}$ M) could be produced from isoprene in ether and a sodium mirror. Stability problems were severe so that no reliable rate constants could be measured. With potassium mirrors, however, active center concentrations up to 4×10^{-4} M could be obtained in short contact times. k_p is appreciably higher than that for lithium based systems, so despite the lower concentration range available, measurements were possible down to −20 °C and at room temperatures down to $\sim 10^{-5}$ M concentrations of active centers. At 18 °C, the derived k_p in-

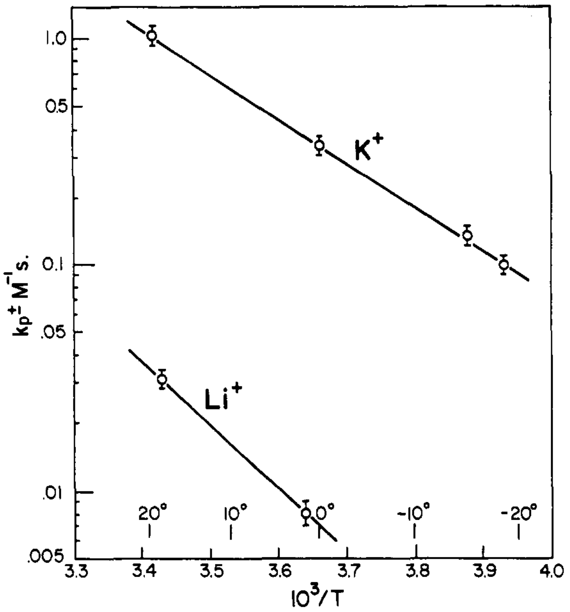

Figure 3. Arrhenius plot of the ion-pair propagation constant for isoprene polymerization in diethyl ether (counterions lithium and potassium).

creased with dilution, as would be expected if free anions were contributing to the rate. The effect is small (slightly greater than a factor of 2 over the above concentration range) and consistent with a very low ion-pair dissociation constant. At 0 °C, no drift with concentration was observed, so single measurements at $c^* \sim 2 \times 10^{-4}$ M were made at lower temperatures. The results are plotted in Figure 3, giving an activation energy of 9.0 kcal mol^{-1} ($A = 5 \times 10^6$). It should be noted that the measurements with lithium as counterion were made in the concentration range *greater* than 3×10^{-4} M. Under these conditions and with an expected ion-pair dissociation constant lower than that for potassium counterion (contact pairs), dissociation effects would be negligible.

Discussion

The optical absorption of I in dilute ether solution occurs at surprisingly long wavelengths compared to those of THF (λ_{max} 287 nm[14]). A similar trend is observed for the polymeric lithium pair. The ^{13}C chemical shifts indicate that charge delocalization is rather less in diethyl ether,[3] so that a shift in the opposite direction might have been expected (e.g., polyisoprenylpotassium in ether, λ_{max} 337 nm). The small fraction of trans centers present in ether but not in THF is unlikely to cause this discrepancy. The corresponding butadiene adduct, neopentylallyllithium,[15] shows an absorption maximum at 310 nm in ether and 290 nm in THF, but in this case the major component is trans in ether and cis in THF and is readily explained on this basis. The absorption maximum of *trans*-I, for example, has been estimated to be 305 nm in THF.[14] In diethyl ether, according to the present experiments cis and trans forms of I do not differ significantly in absorption maximum.

The presence of absorption in the 260-nm region at higher concentrations of I and its polymeric analogues has parallels with other solvent systems. The first effect of addition of THF to a hexane solution of polyisoprenyllithium is to move the maximum from 272 to 262 nm at about 10 molecules of THF per active center.[16] Some association is almost certainly present under these condition.[13,17] Since even smaller amounts of dioxane cause isomerization to the cis form,[18] the associates are likely to be in this configuration in the THF/hexane solutions. Similar effects are observed on addtion of very small amounts of tetramethylethylenediamine[19] (<1 molecule per active center, λ_{max} 265 nm). Evaporation of solvent from an ether solution of the 1:1 adduct of *n*-butyllithium and isoprene followed by repeated replacement by heptane gives a solution of absorption maximum at 265 nm.[20] One or two molecules of ether will be retained in this process leaving ether-solvated aggregates. There is therefore ample evidence for active centers probably in the cis form and associated to some extent absorbing near 260 nm.

Table I
Microstructure of Polyisoprene Produced in Ether at ~20 °C

counterion	% 1,4[a]	% 1,2[a]	% 3,4[a]
Li+	35 (7, 14)	13 (17, 18)	52 (76, 68)
Na+	17 (9)	22 (12)	61 (78)
K+	38 (38, 36)	19 (12, 14)	43 (50, 50)
Cs+	52 (47)	16 (12)	32 (41)

[a] Numbers in parentheses are from ref 20 and 21 for polymerizations in dioxane.

The polymers produced in diethyl ether with all counterions contain appreciable amounts of 1,4 structures (Table I). These appear to be mainly in the trans form even though an accurate determination of the cis/trans ratio was not possible. Similar results have been reported for polyisoprenes prepared in dioxane.[21,22] The largest differences in microstructure between the two solvents occur for lithium and sodium counterions where specific peripheral solvation might be expected to be the strongest. Vinyl addition occurs to a considerable extent, as in most anionic polymerizations in polar solvents. This has been qualitatively attributed to a higher negative charge density at the 3-carbon of the active center than is found in hydrocarbon solvents.[2] Other factors must, however, be important, for on this basis the larger alkali metals would be expected to give polymers with the highest vinyl content. In both dioxane and diethyl ether, the reverse is true.

Attempts to correlate the cis/trans ratio of the 1,4 units in the polymer with the preferred configuration of the active centers meet with problems in isoprene polymerization in polar solvents. The presence of 1,2 units in the polymer indicates that besides structure a ($\sim CH_2CHC(CH_3)CH_2\cdot$metal) whose cis/trans preference has been measured, structure b ($\sim CH_2C(CH_3)CHCH_2\cdot$metal) occurs. "1,4" units in the polymer can be formed from either type of center since ^1H NMR analysis does not distinguish between 1,4 and 4,1 units. If the stable form of both a and b type centers is cis, but the immediate product of monomer addition is a new trans active center which does not have time to reorganize before the next monomer adds, the microstructure is likely to be trans in the 1,4-polymer units. Such a situation has been recognized in butadiene polymerization in the THF at low temperatures.[6] Changes in apparent activation energy and optical absorption at low temperatures could be associated with "freezing-in" of the cis–trans equilibrium of the active centers. This explanation seems less likely to be valid in the present case since a higher temperature range had to be used and no changes of the above type were noticed. If structure b however prefers the trans configuration, many of the 1,4 units in the polymer could be produced from it. All of the evidence on active center structure presented so far relates to structure a. One suggestive piece of evidence exists on structure b formed in a minor amount in the addition of *tert*-butyllithium to isoprene in benzene. If the isoprene is enriched in ^{13}C at the 1 position,[23] moderately strong signals should be observable from the 4-carbon of b. (The strongest signals will of course be produced from the 1-carbon of a.) In THF, the ^{13}C NMR spectrum of enriched I shows a strong signal at $\delta_{\mathrm{Me_4Si}} = 57.4$ ppm and a weaker one at $\delta_{\mathrm{Me_4Si}} = 48.2$ ppm, neither strong enough to be visible in preparations made using normal isoprene. These can be plausibly assigned to trans and cis 4-carbons respectively of structure b with trans predominating, using chemical shift correlations developed by Dorman et al.[24] Further work on b is clearly necessary, but the possibility that significant amounts of trans-1,4 units (as well as 1,2 units) in the polymer are produced from "reversed addition" active centers in polar solvents must be recognized.

The increase in rate of propagation with counterion size in diethyl ether is typical of diene polymerization in polar solvents and is the behavior expected of contact pairs. The principal cause is a decrease in activation energy. Once again it should be noted that two types of active center can occur in polar solvents which may have different reactivities toward monomer. If their proportion varies with counterion, this also could affect relative polymerization rates.

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Self-Stereoselective Polymerization of Racemic β-Chloroalkyl-β-propiolactones in the Solid Phases on Irradiation

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Received May 4, 1979

ABSTRACT: Ring-opening polymerizations of racemic β-dichloromethyl-β-propiolactone (DCPL) and racemic β-trichloromethyl-β-propiolactone (TCPL) in the solid phases on γ-ray or X-ray irradiation provide important information upon the effect of the monomer crystal lattices on the solid-state polymerizations, especially on the propagation step of polymerizations. Racemic DCPL and TCPL both form achiral crystals of the space group $P2_1/b$; two rectus (R) and two sinister (S) molecules in the unit cell compensate the optical activity. However, unlike isotactic poly(DCPL) and atactic poly(TCPL) obtained in solutions with organometallic catalysts, the racemic DCPL and TCPL crystals undergo solid-state polymerization to form new crystalline polymers, most likely syndiotactic poly(DCPL) and isotactic poly(TCPL). The distinct self-stereoselective polymerizations in both crystals are explainable in terms of the effect of the manner of molecular packing in the monomer crystals on the propagation of polymerizations. No detectable polymer is obtained from racemic β-monochloromethyl-β-propiolactone. Classification of solid-state polymerization modes for such racemic monomers is presented.

To date, extensive studies on radiation-induced solid-state polymerizations of a variety of cyclic monomers have been reported. We have investigated solely from the structural viewpoint characteristic features of the solid-state polymerizations of cyclic oligomers of formaldehyde $(\text{-CH}_2\text{O-})_m$, where $m = 3$,[1] 4,[1,2] 5,[3,4] and 6,[5] diketene,[6] and β-propiolactone.[7] These monomers in the single-crystal states have been shown to yield three-dimensionally-oriented or uniaxially-oriented crystalline polymers on γ-ray or X-ray irradiation; the morphological structures of the resulting polymers, such as orientation of polymer chains and twin structure of polymer crystallites, reflect individually the crystal structures of the monomers. The process of "solid-state polymerization" is, however, complicated. It involves initiation, propagation, and termination steps of polymerization, and subreactions if they exist, followed by aggregation (crystallization) of polymer chains in a restricted environment. Therefore, we have been unable to obtain direct evidence concerning the way in which the propagation of polymerization may take place in the crystals at the molecular level. Two contrasting ideas are that (1) propagation of polymerization is really subjected to a monomer crystal lattice control and (2) that propagation takes place at local defect

0024-9297/79/2212-0822$01.00/0