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Articles

Anionic Polymerization of 1,3-Butadiene to Highly Crystalline High *trans*-1,4-Poly(butadiene) with Potassium Catalysts Generated from an Alkyllithium and Potassium *tert*-Amyloxide

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ABSTRACT: Potassium *tert*-amyloxide/*n*-butyllithium affords entry into effectively the same 1,3-butadiene polymerization system as had previously been found for potassium *tert*-amyloxide/alkylmagnesium compounds. Entry can also be achieved through potassium metal/potassium *tert*-amyloxide in the presence of 1,3-butadiene. The operant catalyst species are thus in all cases potassium-based rather than lithium-(or magnesium-)based and are produced by metal–metal exchange in the alkyllithium (and alkylmagnesium) cases or, in the case of potassium metal, by its direct reaction with 1,3-butadiene. The most striking feature of this system is the production (under the right conditions) in high conversion of high *trans*-1,4-poly(butadiene) resin through what must be taken to be anionic polymerization. The formation as well of a medium-vinyl poly(butadiene), which, unlike the highly crystalline high *trans*-1,4-poly(butadiene), is soluble in the hexane reaction medium, is always observed. It is the presence of additional potassium *tert*-amyloxide, beyond that consumed in the metal–metal exchange, that brings about the formation of the high trans-1,4 polymer. The catalyst that generates the high trans-1,4 polymer thus has potassium *tert*-amyloxide coordinated to it in some manner whereas that which generates the medium-vinyl polymer does not. Attempts thus far to prepare block copolymers having high *trans*-1,4-poly(butadiene) blocks have failed, which suggests that this anionic polymerization is not a truly living one.

Introduction

In the companion paper[1] we report that a catalyst that brings about the anionic polymerization of 1,3-butadiene to high (>96%) *trans*-1,4-poly(butadiene) may be generated from alkylmagnesium compounds and potassium *tert*-amyloxide. It was surmised that the actual catalyst is a potassium species, with the alkylmagnesium compound serving merely to alkylate potassium (mg denotes a single magnesium valence).

$$\mathrm{Rmg} + \mathrm{KOAm^t} \rightarrow \mathrm{RK} + \mathrm{mgOAm^t} \qquad (1)$$

Organopotassium compounds are known to initiate anionic polymerization of 1,3-dienes, including butadiene.[2]

Equation 1 is the magnesium analogue of the better known Schlosser–Lochmann–Lim synthesis of potassium (or other alkali-metal) organometallics from a metal alkoxide and an alkyllithium.[3]

$$\mathrm{RLi} + \mathrm{KOR'} \rightarrow \mathrm{RK} + \mathrm{LiOR'} \qquad (2)$$

Therefore, if the catalyst responsible for the generation of high *trans*-1,4-poly(butadiene) is generated as surmised above, alkyllithium compounds should serve in lieu of alkylmagnesiums. The more straightforward and better understood chemistry of lithium here could then facilitate characterization of the catalyst species.

Experimental Section

The protocol here was essentially the same as that for the work with organomagnesium compounds[1] but with the substitution of *n*-butyllithium (2.5 M in hexane; Aldrich) for the organomagnesium compounds. Polymerizations were carried out and worked up in the same manner. Premixes were scrupulously purified, as had been found crucial in the magnesium work, and the potassium *tert*-amyloxide was rectified with potassium metal.

This rectification procedure provided a ready entry into the potassium metal/potassium *tert*-amyloxide/butadiene system. A 32-oz. polymerization bottle containing (the usual) 800 mL of purified butadiene/hexane solution (18.9% butadiene) was charged with potassium sand from a rectification bottle, along with 5.0 mL of the associated *tert*-amyloxide solution (0.89 M). The bottle was mechanically shaken for 3 days. By that time, the bottle contained a fair amount of *trans*-1,4-poly(butadiene) resin in the form of discrete pieces. The viscosity of the solution had increased as well. Potassium metal was still present, embedded in resin. Shaking was continued at room temperature for a total of 6 days. The remaining potassium metal was destroyed by the cautious addition of *tert*-amyl alcohol. Workup in the usual manner yielded 17% conversion to *trans*-1,4-poly(butadiene), the balance to medium-vinyl poly(butadiene).

Geometrical isomerization of high *trans*-1,4-poly(butadiene) was carried out photolytically with the aid of diphenyl disulfide.[4] A 3.0-g sample of the resin from exp 24 of Table I was dissolved in 300 mL of *o*-dichlorobenzene at the boiling point (179–180 °C) and the solution allowed to cool partially before 2.0 g of diphenyl disulfide was dissolved in it. The mixture was allowed to cool to room temperature; a continuous gel resulted. This was irradiated, under nitrogen atmosphere, in a Rayonet reactor for 6 h; some heating occurred in the reactor. At room temperature, the reaction mixture was filtered through nylon mesh to remove gel and added dropwise to several volumes of methanol (containing BHT) to precipitate the polymer. The recovered polymer, 2.5 g or 83%, was characterized (exp 25, Table I).

Gel permeation molecular weights for soluble poly(butadienes) were determined as in the organomagnesium work, and both

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Table I
Butadiene Polymerizations with $KOAm^t/n$-BuLi Catalyst[a]

			trans-1,4-PBd		soluble poly(butadiene)									
								1000's				microstructure, %		
exp	n-BuLi,[b] mmol/100 g of Bd	K/Li	conv, %	T_m, °C	conv, %	T_g, °C	M_w/M_n	M_w	M_n	M_n(Li)[c]	$M_n(\mathrm{Li})/M_n$ (chains/Li)	vinyl	trans	cis
1	0.5	2.0	93	67, 151	3									
2	0.5	3.0	98	68, 150	2									
3[d]	0.5	3.0[d]	0		39	−29	2.13	172	81	76	0.94	80	15	5
4	0.5	1.0	0		99	−56	1.46	279	191	195	1.02	52	36	12
5	0.5	1.3	0		100	−56	1.32	244	185	201	1.09	53	36	11
6	0.5	1.4	25		68	−58	1.68	311	167	128	0.77	52	36	12
7	0.5	1.6	69		30	−59	2.32	139	60	56	0.93	54	33	13
8	0.5	1.8	44	76, 152	56	−56	2.31	209	91	106	1.19	55	33	12
9	0.5	2.0	37		63	−55	1.92	173	90	119	1.32	56	32	12
10	1.0	6.0	72		28	−59	2.45	344	140	23	0.16	56	29	15
11	1.0	6.0	61		39									
12[e]	0.5	6.0	80		20									
13[f]	0.5	5.0	43	73, 152	3									
14[f]	0.5	10.0	13	67, 152	2									
15[f]	0.5	20.0	29	67, 152	4									
16[g]	0.5	6.0	3	76, 138	89	−70	2.43	69	28	170	6.07	44	37	19
17[g]	0.5	6.0	10	75, 124	73									
18[h]	0.5	6.0	87	68, 150	13									
19[i]	1.0	6.0	36		62	−61								
20	0.5	6.0	91		9	−59								
21	0.5	1.0/6.0	48		54	−59	1.35	108	80	107	1.33	52	37	11
22	0.5	1.0/6.0	19		77	−57								
23	0.5	6.0	93		7									
24	0.5	6.0	40		7									
25	24 exp resin isomerized			25	83	−87	3.53	349	99	85	0.86	0	79	21

[a] Unless noted otherwise, in hexane at 10 °C (charged at room temperature) for 18 h or more. [b] Approximately, owing to some variation in butadiene concentration in premixes; conversions and M_n(Li) values based on actual amounts. [c] Grams of soluble polymer obtained per moles of Li charged. [d] $NaOAm^t$ instead of $KOAm^t$. [e] Potassium *tert*-amyloxide solution not treated with potassium metal. [f] Shortstopped after 45 min at 10 °C. [g] Polymerization at 50 °C (charged at room temperature). [h] Polymerization allowed to proceed without cooling after charging at ambient temperature (exotherm). [i] *tert*-Butyllithium used instead of *n*-butyllithium.

nuclear magnetic resonance and infrared spectra were obtained as in that work.

Results and Discussion

As the data in Table I show, butyllithium in tandem with potassium *tert*-amyloxide can serve as an efficient generator of the catalyst producing high *trans*-1,4-poly(butadiene). Monomer conversions to this polymer of more than 90% can be attained. The catalyst system generated via an alkyllithium is effectively indistinguishable from that generated with an alkylmagnesium cocatalyst. Thus partitioning, as typically seen with alkylmagnesium cocatalysts, of the product polymer between high *trans*-1,4-poly(butadiene), insoluble by virtue of its high degree of crystallinity, and soluble, medium-vinyl poly(butadiene) is seen also with alkyllithium cocatalysts. Sensitivity of this partitioning to overall system purity holds for both types of cocatalyst.

Within experimental error, the microstructure of both poly(butadienes) is independent of cocatalyst type. This is strong evidence that all catalyst species operant here are potassium-based, with lithium or magnesium, as the case may be, playing at most a peripheral role beyond catalyst generation. However, even a peripheral role is ruled out by our finding (see the Experimental Section) that entry into this catalyst system may be had using only potassium metal sand, butadiene monomer, and potassium *tert*-amyloxide (hexane solvent).

As noted above, anionic polymerization of butadiene with potassium-based catalysts is known.[2] However, the production of high *trans*-1,4-poly(butadiene) by such catalysts is unique to those generated here, as well as in the earlier work with alkylmagnesium compounds,[1] via alkylation of potassium *tert*-amyloxide or at least, in view of the present result with potassium metal, in the presence of the *tert*-amyloxide.

Clues to the role of potassium *tert*-amyloxide and the nature of the catalyst species are to be found in the response of the system to the K/Li mole ratio. Potassium-based catalyst is here taken to be generated by potassium–lithium exchange in a Schlosser–Lochmann manner, either to generate an alkylpotassium per eq 2 followed by the initiation of polymerization by the alkylpotassium

$$RK + nBd \rightarrow R(Bd)_nK \qquad (3)$$

or, insofar as initiation of polymerization by alkyllithium has occurred, to convert any lithium species so produced to potassium ones.

In any case, the K/Li stoichiometry in such exchanges is 1/1, if, as is normally the case,[3] the exchange goes to completion. However, a K/Li mole ratio of unity here does not suffice to produce any high *trans*-1,4-poly(butadiene); the product is exclusively medium-vinyl poly(butadiene). In the present work, no high *trans*-1,4-poly(butadiene) was produced at K/Li mole ratio 1.0 or 1.3 (exp 4 and 5, Table I). In the range of K/Li mole ratio 1.4–2.0, mixtures containing substantial fractions of both medium-vinyl and high *trans*-1,4-poly(butadiene) were produced (exp 6–9, Table I). That the product partitioning does not correlate monotonically with the K/Li mole ratio in this range, and indeed does not reproduce well in ostensibly replicate experiments at mole ratio 2.0 (exp 1 and 9, Table I), is ascribed to the high sensitivity of the system to adventitious impurities.

Nonetheless, conversions to high *trans*-1,4-poly(butadiene) of the order of 90% are not seen below K/Li mole ratio 4.0; the indication is strong that potassium *tert*-amyloxide beyond the mole needed to potassium–lithium exchange is required for the generation of high *trans*-1,4-poly(butadiene). Lochmann has recently presented compelling evidence that potassium alkoxides, in contrast to lithium alkoxides, complex with alkylpotassiums.[3a] Complexation of potassium *tert*-amyloxide with the potassium polymerization locus is to be expected from these results of Lochmann.

It is worth stressing that at intermediate K/Li ratios one does *not* see polymer of microstructure intermediate between the medium-vinyl and high trans-1,4 microstructures; the product ratio varies, but the two components do not vary intrinsically in microstructure. Thus polymerization loci producing a given microstructure apparently do not convert to the alternative type (which could conceivably occur by exchange of potassium *tert*-amyloxide), at least not at a rate competitive with butadiene polymerization.

The data in Table I also suggest that higher catalyst concentration (exp 10 and 11) shifts the product mix in the direction of favoring the medium-vinyl polymer (although this could perhaps be ascribed to a higher impurity level at the higher catalyst level).

The medium-vinyl poly(butadiene) whose formation is favored by inadequately purified systems is, by microstructure,[1] the same one produced at low potassium *tert*-amyloxide/alkyllithium molar charge ratio. Since impurities such as water or oxygen should effectively raise this ratio by replacing metal–carbon (lithium and/or potassium) with metal–oxygen bonds, it might have been expected that higher impurity levels (so long as the catalyst is not destroyed altogether) would favor the production of high *trans*-1,4-poly(butadiene). However, the opposite (e.g., exp 12, Table I) is the case. Further, even high potassium *tert*-amyloxide/alkyllithium ratios do not suppress the formation of medium-vinyl poly(butadiene) and in fact appear to retard the formation of high *trans*-1,4-poly(butadiene) somewhat (exp 13–15, Table I). More detailed studies of the effects of impurities are needed.

At 50 °C (exp 16 and 17, Table I), the polymerization system exhibits the same general features as at 10 °C, namely, production of both an isoluble *trans*-1,4-poly(butadiene) and a soluble poly(butadiene) of mixed microstructure. DSC data for the insoluble polymer indicated it to be of lower 1,4-trans content than the corresponding material produced at 10 °C, but the difference is not marked. The microstructure of the soluble poly(butadiene) produced at 50 °C differs from that produced at 10 °C in having, not unexpectedly, more nearly equal percentages of all three microstructural types.

Polymerizations at 50 °C favored formation of the soluble poly(butadiene) over that of the 1,4-trans material. However, total monomer conversions at 50 °C were lower than the essentially 100% achieved in polymerizations at 10 °C of sufficient duration. These observations, as well as the pattern seen in the polymerizations at 50 °C with alkylmagnesium-generated catalysts[1] of lower total conversion at higher conversion to *trans*-1,4-poly(butadiene), suggest that the catalyst producing the 1,4-trans material eventually becomes deactivated at 50 °C. The more of the catalyst that is diverted toward the production of 1,4-trans material and subsequently inactivated, the less that remains to produce the soluble poly(butadiene). It is possible that the deactivation at 50 °C of the catalyst producing 1,4-trans material is not so much chemical as it is physical, a result of the coalescence of the 1,4-trans material at 50 °C, thereby entrapping and monomer-starving the catalyst.

SEC molecular weight data for some of the soluble poly(butadienes) produced here are found in Table I. These measured M_n values are compared with those calculated on the basis of one polymer chain generated per lithium atom charged, i.e., grams of soluble polymer per mole of Li. For polymerizations done at 10 °C, there is good agreement between the measured and calculated M_n values in cases where the product polymer is entirely soluble poly(butadiene) (low K/Li mole ratio plus an instance where sodium rather than potassium *tert*-amyloxide was used; exp 3–5, Table I). These data are thus consistent with conversion of all of the alkyllithium to an equivalent amount of potassium-based polymerization loci with butadiene polymerization to the soluble, medium-vinyl poly(butadiene) on a basis of one polymer chain per polymerization locus.

If the soluble poly(butadiene) were to continue to be formed on this basis in systems with a higher K/Li ratio where high *trans*-1,4-poly(butadiene) is also formed, the M_n for the soluble polymer and the actual catalyst level would remain inversely proportional and the calculated/measured M_n ratio for the soluble poly(butadiene) would thus correspond to the *fraction* of the polymerization loci used to generate the soluble polymer. In polymerizations carried out at the lower K/Li ratios at which the trans polymer is seen (exp 6 and 7, Table I), this M_n ratio is indeed less than unity. However, this M_n ratio increases as the K/Li ratio increases and ultimately exceeds unity, which requires more than one chain of soluble polymer to have been generated per polymerization locus derived by potassium–lithium exchange, even if 100% of these loci generated soluble polymer. Surely even before the M_n ratio has exceeded unity, more chains of soluble polymer have been formed than could be accounted for on the basis of the fraction of the loci derived by potassium–lithium exchange involved in generation of the soluble polymer.

If, however, the calculated M_n is based on the total amount of *potassium* in the system rather than the total amount of lithium, calculated/measured M_n ratios above unity are not seen. That is, although the limit of one chain of soluble polymer per lithium is often exceeded, that of one chain per potassium never is. In systems where substantial high *trans*-1,4-poly(butadiene) is formed, the M_n ratio based on potassium is less than unity, presumably reflecting the diversion of some polymerization loci to the generation of the trans polymer. If successful, systems with still higher K/Li ratios generate, at 10 °C, mostly high *trans*-1,4-poly(butadiene). This is not true at 50 °C, and for an example at that temperature (exp 16, Table I) M_n for the soluble polymer (formed almost exclusively) corresponds closely to the value based on the total amount of potassium, which is only *one-sixth* that based on the total amount of lithium.

Potassium *tert*-amyloxide, beyond the mole alkylated by the alkyllithium, thus appears to be capable of involvement in the generation of polymerization loci on the basis of one locus per potassium *tert*-amyloxide moiety so involved. Two possibilities here are as follows:

(1) Initiation of polymerization by potassium *tert*-amyloxide, in addition to the initiation by alkylpotassium (or alkyllithium). Attempts to initiate polymerization with potassium *tert*-amyloxide alone here gave negative results, even at 50 °C. Nonetheless, it is still conceivable that an organopotassium, e.g., the polymerization locus, could bring about initiation by the *tert*-amyloxide.

(2) Chain transfer: The most straightforward mode of chain transfer here entails, at least formally, the elimination of potassium hydride from the polymerization locus and its addition to monomer. Although potassium *tert*-amyloxide might facilitate such a process, it is not immediately obvious how it would thereby be consumed, which the constraint of only one new polymer chain per

Table II
Butadiene Polymerizations Initiated with *n*-BuLi/TMEDA (TMEDA/Li = 2), with Subsequent Addition of KOAm^t

				soluble poly(butadiene)									
							1000's				microstructure, %		
exp	$\mathrm{Bu}^n\mathrm{Li}$,[a] mmol/ 100 g of Bd	K/Li	*trans*-1,4-PBd: conv, %	conv, %	T_g, °C	M_w/M_n	M_w	M_n	M_n(Li)	$M_n(\mathrm{Li})/M_n$[b]	vinyl	trans	cis
1[c]	1.0	4.0	0	100	−38	1.18	106	90	97	1.08	74	16	10
2[d]	1.0	4.0	44	56	−44	1.26	64	51	59	1.16	73	17	10
3[d]	1.0	4.0	28	72	−52	1.30	51	39	71	1.82	70	19	11

[a] Based on total monomer. [b] Average number of polymer chains per lithium charged. [c] Polymerization with $\mathrm{Bu}^n\mathrm{Li}$/TMEDA at 50 °C for 60 min, followed by cooling in a 10 °C bath and then injection of KOAm^t. [d] As in footnote *c* but for 200 min before cooling, and then charging of the second half of the monomer and injection of KOAm^t.

potassium *tert*-amyloxide moiety implies.

A prime impetus for the development of an anionic polymerization route to high *trans*-poly(butadiene) was the hope that this polymer could thereby be incorporated into a variety of block copolymers, as has been done for other anionically attainable hydrocarbon polymers. The difference in behavior of the polymerization system at 10 and at 50 °C noted above is such that changing the temperature during the polymerization would likely not be fruitful here. An alternative apparently straightforward way, in view of the dependence of poly(butadiene) microstructure on the alkoxide/alkyl ratio, to prepare at least diblock copolymers from butadiene monomer alone, would be to initiate polymerization at a low alkoxide/alkyl ratio and then to subsequently raise the ratio at some intermediate monomer conversion by the addition of additional potassium *tert*-amyloxide. However, the result of such attempts (exp 21 and 22, Table I) was invariably the production of mixtures rather than block copolymers of medium-vinyl and high *trans*-1,4-poly(butadienes); no block copolymer could be detected. Phenomena that could account for this failure include the following:

(1) Polymerization to medium-vinyl poly(butadiene) entails chain transfer to monomer.

(2) Polymerization to high *trans*-1,4-poly(butadiene) entails chain transfer to monomer.

(3) Conversion of the potassium polymerization locus to the form yielding high *trans*-1,4-poly(butadiene) by complexation with potassium *tert*-amyloxide entails a chain transfer to monomer.

The polymer molecular weight data discussed above indicate it is unlikely that the polymerization to medium-vinyl poly(butadiene) at a low alkoxide/alkyl charge ratio entails much chain transfer. The picture is less clear for the polymerization to high *trans*-1,4-poly(butadiene) at high alkoxide/alkyl charge ratio. Owing to its insolubility, molecular weight data were not obtained for the *trans*-1,4-poly(butadienes). However, the very low solubility and general properties of the material suggest a substantial molecular weight, perhaps indeed commensurate with the monomer/catalyst ratios used. SEC molecular weight data for a sample isomerized to a soluble microstructure did yield an M_n that corresponds fairly closely to that expected on the basis of one polymer chain per lithium atom charged (exp 25, Table I). Thus, chain transfer may well not be significant in this polymerization either. However, these molecular weight data are not unequivocal, largely because of uncertainty about the true catalyst levels.

A variant of the above approach to diblock copolymer preparation was tried in which the polymerization to soluble poly(butadiene) was carried out under the aegis of a lithium catalyst. Collected in Table II are the results of some in situ additions of potassium *tert*-amyloxide to lithium-catalyzed butadiene polymerizations. TMEDA-complexed lithium catalyst (TMEDA/Li = 2.0) was employed in order to ensure complete involvement of the lithium catalyst in initiation of polymerization fairly early on,[5] certainly by the point at which the potassium *tert*-amyloxide was added (the TMEDA should have little effect on the polymerization thereafter[1]). The lithium-based polymerization should proceed without transfer or termination. Thus, ideally, all of the carbon-bound lithium should be in the form of macromolecular terminal allylic species upon the conversion to potassium-based polymerization. In the absence of further complications, a medium-vinyl PBd/*trans*-1,4-PBd diblock copolymer would be expected to result.

In one of the experiments here (exp 1, Table II), the potassium *tert*-amyloxide was added at an arbitrary point, where it was estimated that some butadiene remained unreacted. In the other two, only half of the butadiene was charged initially; the second half was charged, followed immediately by the potassium *tert*-amyloxide, after it could be safely assumed that polymerization of the initial monomer charge was effectively complete (exp 2 and 3, Table II).

As it turned out, the first experiment apparently had the potassium *tert*-amyloxide added too late, after the butadiene had been essentially completely polymerized. However, it thus serves as a control for the other two experiments. There, rather than block copolymers, mixtures of soluble and *trans*-1,4-poly(butadiene) resulted. The soluble poly(butadiene) in turn is apparently comprised of two components, a higher vinyl polymer due to the lithium-catalyzed polymerization[5] and the medium-vinyl polymer associated with the potassium-based polymerization, here represented by the difference between 50% and the conversion to the trans resin. The lower T_g values and vinyl contents for the soluble polymer in these two experiments, while consistent with this, could also arise from block copolymers comprised of the two vinyl contents. However, the increased $M_n(\mathrm{Li})/M_n$ values, particularly for the one with the lower conversion to resin (exp 3), are a strong indication of a mixture of soluble polymers and not a block copolymer.

In short, the results of these experiments are consistent with the simple superimposition of a potassium-based polymerization to *trans*-1,4-poly(butadiene), and the invariably associated medium-vinyl poly(butadiene), upon the prior lithium-based polymerization. The lithium serves merely to generate the potassium-based catalyst, just as if it had not participated in the prior polymerization. It would seem then that either the generation of the potassium catalyst occasions a chain-transfer event or that transfer occurs fairly often with the potassium-based polymerization (or both, of course; another possibility, though unlikely, is that the monomer-starved macromolecular lithium species decay, producing low molecular weight lithium moieties, prior to the advent of the potassium).

Work with this catalyst system and monomers other than butadiene is incomplete and is not dealt with in this

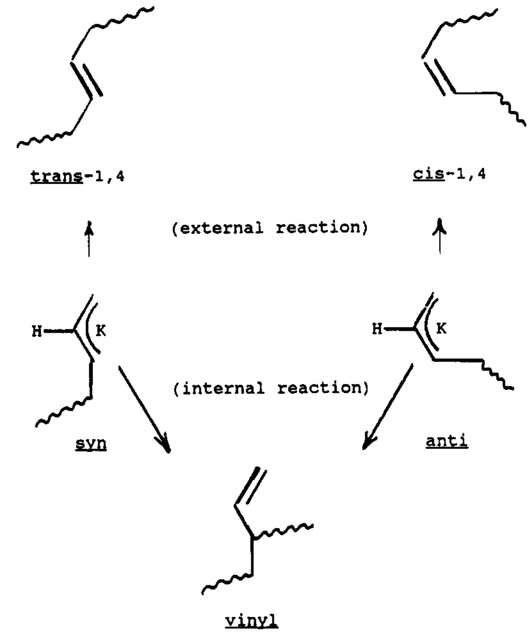

Figure 1. Options for the reaction of macromolecular allylic potassium species with butadiene monomer.

paper. It may be mentioned, for example, that styrene is consumed more rapidly, although far from exclusively, in styrene/butadiene copolymerizations and the microstructure of the copolymerized butadiene units resembles that of the soluble poly(butadiene) obtained in butadiene homopolymerizations with respect to the percentages of each microstructural type. Moreover, when the styrene charge level is low enough for it to be virtually completely consumed while substantial butadiene remains, this butadiene is then largely converted to high *trans*-1,4-poly(butadiene). Once again, block copolymer is not seen.

Conclusions

Effectively the same catalyst system may be generated by alkylation of potassium alkoxide/butadiene by either alkylmagnesium or alkyllithium compounds or by the reaction of potassium metal/butadiene/potassium alkoxide. Salient features of this system are as follows:

(1) Two general types of polymerization locus may be operant here; one type is responsible for high trans-1,4 and the other for medium-vinyl poly(butadiene).

(2) Both types of polymerization loci are potassium-based; metal ions of organolithium (or magnesium) agents used to generate the requisite potassium–carbon bonds are not involved in the polymerization loci.

(3) Polymerization loci that generate high *trans*-1,4-poly(butadiene) have (at least) equivalent associated potassium *tert*-amyloxide; those that generate medium-vinyl poly(butadiene) do not. Potassium *tert*-amyloxide irreversibly converts the type of locus that yields medium-vinyl poly(butadiene) to the type that yields high *trans*-1,4-poly(butadiene).

The microstructural outcome for polymerization loci yielding the medium-vinyl poly(butadiene) here is reminiscent of that obtained with other potassium-based polymerizations in similar media.[2] The polymerization loci are taken to be allylic potassium species that may be viewed as being fairly ionic. Such a locus may exist in either the syn or the anti form and may react at either the external or the internal allylic terminus (Figure 1). Reaction with monomer at the external terminus to yield a new allylic species results in the incorporation of a *trans*-1,4-poly(butadiene) penultimate unit if the syn form and a *cis*-1,4-poly(butadiene) penultimate unit if the anti form. Reaction at the internal terminus of either the syn or the anti form results in the incorporation of a 1,2-poly(butadiene) penultimate unit.

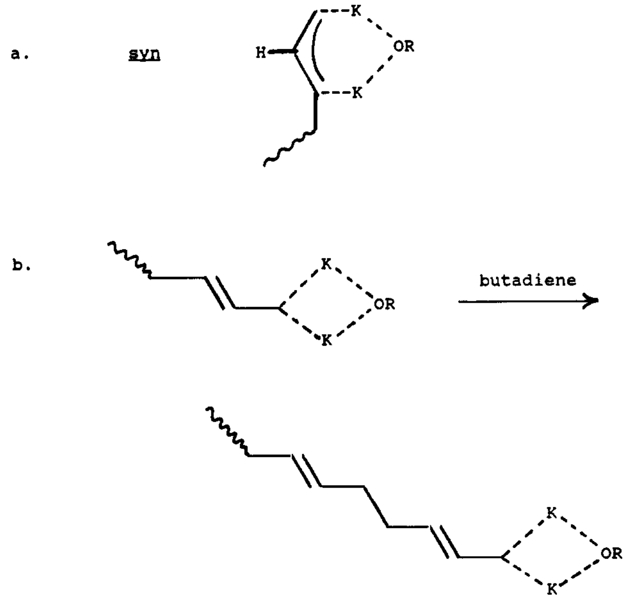

Figure 2. (a) Possible complexation of potassium *tert*-amyloxide with allylic potassium species. (b) Reaction of trans monodentate allylic species to incorporate a *trans*-1,4-PBd unit and form a new trans monodentate allylic species.

Thus, the polymerization loci yielding the soluble poly(butadiene) here exhibit significant reaction through both the syn and the anti forms (at the external terminus of both and at the internal terminus of at least one of them), resulting in the formation of poly(butadiene) of mixed microstructure. Substantial reaction at both termini is not unexpected since there is substantial negative charge at both. The extent to which reaction through the syn versus the anti form derives from thermodynamic or equilibrium factors on the one hand and kinetic factors on the other[6] is not entirely clear. For a potassium-based polymerization the work of Bywater and colleagues[6] would suggest that the allylic anion is initially formed with the syn geometry and that isomerization to the anti form competes with reaction with monomer.

The dramatic change in the microstructural outcome upon complexation of the polymerization locus with potassium *tert*-amyloxide corresponds, then to almost exclusive reaction through the external terminus of the syn form, resulting in the almost exclusive incorporation of trans-1,4 units. While potassium *tert*-amyloxide can be envisaged as being incorporated into a coordinated structure such as that shown in Figure 2a, it is not immediately obvious why such a structure should engender the observed microstructural consequences. Possibly the bonding to two potassium cations as shown hinders monomer access to the internal terminus of the allylic anion and, again, for either kinetic or equilibrium reasons[6] reaction occurs through the syn form (shown) only.

An alternative possibility is that *tert*-amyloxide partially displaces the allyl anion from the coordination sphere of potassium, rendering the anion monodentate. A structure having this feature is shown in Figure 2b. In such a structure, postulated here to be favored over that having the potassium cations coordinated to the internal terminus, charge is largely localized on the external terminus, which should result in almost exclusive 1,4 incorporation. The geometry of the here largely localized double bond in the allyl anion, which corresponds to the geometry of the poly-

(butadiene) unit to be produced from it, is shown as trans. This could well be the geometry initially formed when butadiene is added to the antecedent allyl species.[6] Reaction with monomer may compete effectively with isomerization (via the form that has the potassiums coordinated to the internal terminus) to the corresponding cis form.[6]

To what extent polymerizations with these anionic potassium-based catalyst systems exhibit the "living" behavior often associated with ostensibly similar anionic polymerizations in the traditional sense[2a] of relatively rapid initiation with propagation without termination or transfer is unclear. The polymerization to medium-vinyl poly(butadiene) here appears at least to be complicated by initiation by more than one species, likely at different rates. Propagation, however, appears to proceed without transfer as evidenced by a general correlation between the catalyst level and the polymer number-average molecular weight, although the actual catalyst levels, to be sure, are equivocal.

In the case of the polymerization to high *trans*-1,4-poly(butadiene), knowledge of the relationship between the catalyst level and the polymer molecular weight is much more nebulous. Little can be said at present beyond the observation that the fairly low catalyst levels used here yield what appears to be fairly high molecular weight polymer, which suggests that transfer/termination is not rampant. However, the failures to incorporate the high *trans*-1,4-poly(butadiene) into block copolymers recounted in this work suggest that propagation here may be complicated to some extent by such phenomena and that this anionic polymerization is thus not truly living.

References and Notes

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Registry No. TMEDA, 110-18-9; KOAm, 41233-93-6; *n*-BuLi, 109-72-8; K, 7440-09-7; *trans*-1,4-PBd (homopolymer), 9003-17-2; *t*-BuLi, 594-19-4.