block polymer. Thus replacement of polystyrene by poly-α-methylstyrene endows the resultant block polymer with both greater tensile strength and higher temperature capability.

At 100° the mSImS-1 block polymer retains a tensile strength of 65 kg cm^{-2}. This polymer is thus markedly stronger than many gum rubber vulcanizates, *e.g.*, SBR[26] $\sim$6 kg cm^{-2}, with the exception of Hevea vulcanizates. The mSImS-1 material is somewhat weaker at 100° than some carbon black filled rubbers, *e.g.*, Hevea[27] ($\sim$180 kg cm^{-2}), a 55/45 butadiene–acrylonitrile copolymer[27] ($\sim$130 kg cm^{-2}), or SBR[28] ($\sim$100 kg cm^{-2}), while on the other hand, it is stronger than such filled vulcanizates as an emulsion polyisoprene[28] ($\sim$55 kg cm^{-2}) or polyisobutylene[29] ($\sim$50 kg cm^{-2}). Thus this block polymer is comparable in breaking stress at 100° to some filled rubber vulcanizates while at ambient temperature and lower it possesses a higher breaking stress than any conventionally cross-linked filled rubber vulcanizate, including the best Hevea vulcanizates.

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Exchange Reactions between Lithium Alkyl and Alkenyl Aggregates in Hydrocarbon Solution

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ABSTRACT: The ^{7}Li nmr spectra of a number of lithium alkyls (*n*-, *sec*-, and *t*-butyl) together with lithiomethyltrimethylsilane and oligomeric polyisoprenyllithium have been measured alone and in binary mixtures in cyclopentane. All the systems showed rapid mixing of the aggregated species at room temperature if *t*-butyllithium was not one of the components. The systems containing *t*-butyllithium behaved differently. Slow mixing of *t*-butyllithium over a period of hours was observed with both *sec*-butyllithium and lithiotrimethylsilane but with polyisoprenyllithium partial exchange occurred in at most a few minutes but did not proceed further. The implications of these experiments for polymerization studies is discussed.

The physical properties of lithium alkyls in solution have a very important bearing on their initiation of polymerization. It is well known that the alkyls are associated in solution in hydrocarbons as are the active centers in polymerization.[2] In the early stages of polymerization both residual lithium alkyl and polymer lithium species will coexist. The formation of mixed aggregates can be expected under these conditions as was demonstrated for simple alkyls by Weiner and West[3a] and for the polymer systems by Morton.[3b] The behavior of lithium alkyl initiators in aliphatic hydrocarbons in particular shows a rather complex pattern. There is a period of increasing initiation rate,[4] most probably linked to reactivity differences of the various alkyl containing aggregates[5] present at different times, before reaction slows due to depletion of the reactants. The process of chain initiation might then be affected by rates of exchange of lithium-containing species between various aggregates or by the dissociation rates of these aggregates. If intermolecular exchange takes place by a dissociative process, as has been suggested,[6] these two processes are related.

The chemical shift of the ^{7}Li resonance is sensitive to the environment in the aggregates and has been used by Brown[7] to measure exchange rates between simple alkyls in a number of solvents. It is of obvious interest to extend these data to systems of interest in polymer chemistry, and for this purpose low molecular weight polyisoprenyllithium was chosen.

Experimental Section

The lithium alkyls used were supplied by the Foote Mineral Co. as solutions in heptane or pentane, with the exception of lithiomethyltrimethylsilane ($LiCH_2Si(CH_3)_3$) which was prepared as described in the literature.[8]

n-Butyllithium was used as received after removal of the solvent. The secondary and tertiary compounds were subjected to a short-path distillation to a cooled receiver. *t*-Butyllithium sublimes smoothly at 75°, *sec*-butyllithium

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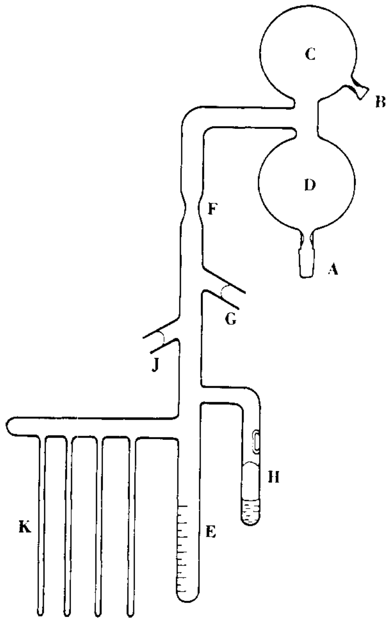

Figure 1. Apparatus for preparing mixtures of lithium compounds under vacuum for nmr analysis.

at 80°, and the silyl compound at 105° under high vacuum conditions. The sealed cold finger was attached to a simpler version of the apparatus described below and diluted under vacuum with the required solvent. The final concentration was about 0.7–0.8 *M*. The mixtures of alkenyl-(polyisoprenyl)lithium and lithium alkyl were prepared in the apparatus shown in Figure 1. This was attached to the vacuum line (inverted) at A. Wash *n*-butyllithium was added by syringe through the serum cap at B which was then sealed off allowing a good vacuum to be attained. Solvent was then distilled in and the apparatus was sealed off near A. The wash solution could then be distributed to remove surface contamination from the glassware. After draining the solution into C the solvent was gently refluxed to remove residual butyllithium from the walls. The solution was next transferred to D and the required amount of dry solvent distilled into E followed by sealing off the unwanted upper portion at F. *sec*-Butyllithium could then be added from the distillation vessel attached at G, and isoprene slowly distilled in after breaking the seal at H. The isoprene/initiator ratio varied between 3.5 and 5, a value more than adequate to consume all the *sec*-butyllithium. The reaction was allowed to stand for 24 hr to ensure complete polymerization, at which time the particular alkyl under investigation could be added from its distillation vessel *via* the break-seal at J. About 5 min were required for mixing, and distributing the solution to the nmr tubes at K and sealing them off. These were then immediately placed in a Dry Ice–acetone bath and stored at low temperature until required for study. The mixtures of alkyls were prepared in a similar way, omitting the isoprene addition. Solvents and isoprene were in general purified as described previously[9] and were stored over calcium hydride on the vacuum line.

The ^{7}Li resonance measurements were carried out on a Varian HR-100 spectrometer at a frequency of 25.14 MHz; the magnetic field was reduced to a value of *ca.* 15.2 kG. The reference signal was supplied from an internal capillary containing 3.5 *M* lithium bromide in methanol. In a few early experiments, 8.8 *M* aqueous LiBr was used as reference.

TABLE I
CHEMICAL SHIFTS OF LITHIUM RESONANCES[a]

	Silyl	*n*-Butyl	*sec*-Butyl	*t*-Butyl	Alkenyl
Cyclopentane	69.5	69.0	52.6	46.0	25.8
Benzene			36.7	31.4	21.2
Cyclohexane			52.0	45.5	

[a] All resonances are downfield in cycles per second from methanolic LiBr.

Chemical shifts have been corrected in these cases to the methanolic standard. It was established that the resonance of the aqueous salt is 24.7 Hz downfield from the alcoholic solution.

Results

The chemical shifts of the various lithium compounds are shown in Table I. In cyclopentane, the alkenyl resonance is at considerably higher field than those of the alkyls, so the system is suitable for a study of mixtures. The resonances in benzene are apparently at higher field, but since bulk magnetic susceptibility corrections were not applied, it is not possible to say if this change has any significance. The line widths of the *sec*- and *t*-butyl compounds were around 2 Hz at room temperature, but that of the *n*-butyllithium was appreciably larger (~6 Hz). This may be an experimental artifact caused by the inability to purify this compound by distillation. Routine analysis of this material by the double titration method, however, has never revealed more than traces of other lithium salts. The polyisoprenyllithium gave also a broader resonance line which could have a half-width of as much as 15 Hz although in some samples it could be as low as 7–8 Hz. In studying mixtures, the spectrum of the actual alkenyl sample used in that particular mixture was used as reference. There was evidence that higher molecular weight samples had a broader resonance line over the range of the degree of polymerization between 3.5 and 5.5. This molecule has however an appreciably higher molecular weight than the alkyls (higher τ_c) and is in fact a mixture of structures, so a wider line is not unexpected.

Most of the mixtures were examined in cyclopentane in order to be able to investigate low-temperature behavior. The behavior in other aliphatic hydrocarbons would be expected to be similar. In many of these systems rapid exchange was indicated at room temperature on the nmr time scale. Only a single symmetrical resonance absorption was observed at a chemical shift close to the weighted average of the components. These systems, in cyclopentane, included the mixtures of polyisoprenyllithium with the *n*-butyl, *sec*-butyl and silyl compounds and *sec*-butyllithium mixed with *n*-butyl or lithiomethyltrimethylsilane. At lower temperatures the lines broadened, more rapidly than did those of the individual components, indicating some slowing of the exchange rate (Figure 2). In some cases the peak became asymmetric (Figure 3) which suggests that had the individual resonances been sharper (particularly that of the alkenyl), individual resonances of mixed aggregates would have been visible. Only with the system *sec*-butyllithium–lithiomethyltrimethylsilane were separate peaks observed at low temperature (Figure 4). Here the single sharp resonance observed

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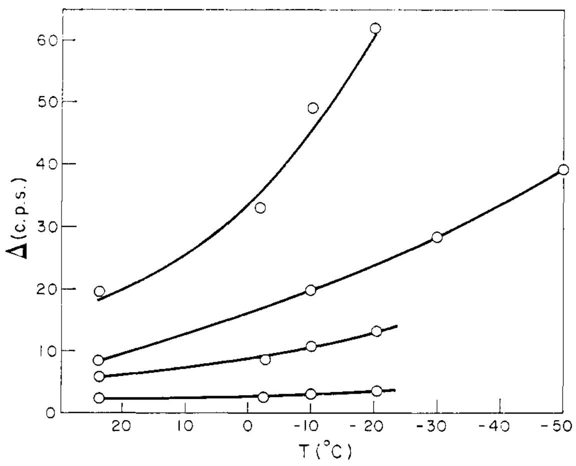

Figure 2. Line widths (Δ) in cyclopentane as a function of temperature. In descending order: (1) alkenyl-*n*-butyllithium mixture, (2) alkenyllithium alone, (3) *n*-butyllithium alone, (4) *sec*-butyllithium alone.

at room temperature broadened on cooling and the *sec*-butyllithium resonance appeared distinctly with only a broader resonance for the silyl-rich species. It appears that the *sec*-butyllithium tetramer is the slower exchanging species under these conditions. The equilibria were reversible and established as rapidly as the cell temperature could be changed.

Three of the systems examined in cyclopentane showed different behavior; all involved *t*-butyllithium. The first was the *t*-butyllithium/lithiomethyltrimethylsilane system in cyclopentane. This is the system previously studied by Brown.[6] We were able to confirm that intermolecular exchange is slow and were able to follow the changes of the original two-line spectrum to a five-line spectrum over a period of several hours at room temperature. The second system was that involving *t*-butyllithium and *sec*-butyllithium. Once again at room temperature the original two signals coalesced slowly over a period of several hours to an asymmetric peak. The chemical shift difference between the two starting materials is only 6.5 Hz so the appearance of separate signals from mixed species could not be expected. The third system involved *t*-butyllithium and polyisoprenyllithium. In this case, the spectrum shown in Figure 5 was obtained within the few minutes required for mixing and observation of the spectrum and which did not change for many hours afterward. Some intermolecular exchange has occurred within the above time period as can be seen from the superimposed spectrum calculated from those of the original components. Rapid intermolecular exchange seems to be taking place between polyisoprenyl-rich species but

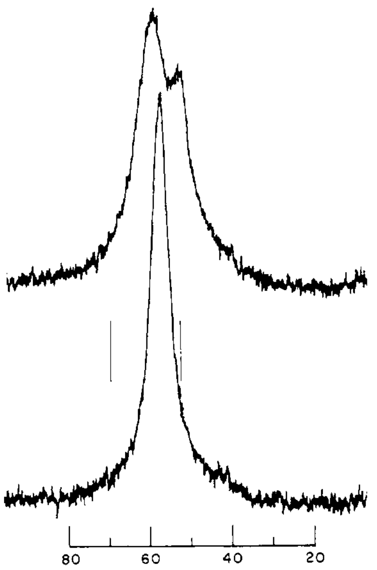

Figure 4. ^{7}Li spectra of a mixture of *sec*-butyllithium–lithiomethyltrimethylsilane (ratio 2/1) in cyclopentane: lower curve, +24°; upper curve, −21°. The two vertical bars show the line positions of the unmixed components. Scale as in Figure 3.

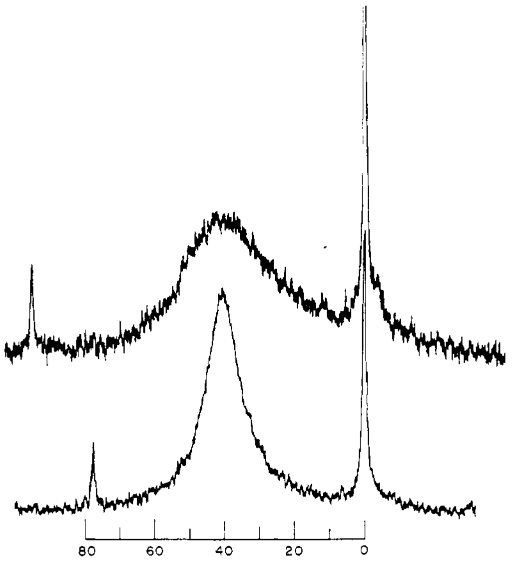

Figure 3. ^{7}Li spectra of a mixture of alkenyl and *sec*-butyllithium in cyclopentane (ratio 0.75/1): lower curve, +24°; upper curve, −2°. Scale, cycles downfield from methanolic lithium bromide.

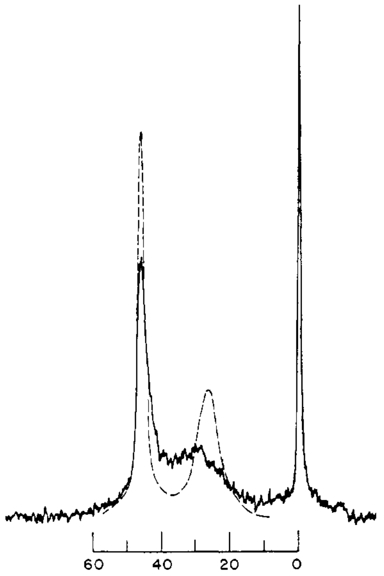

Figure 5. ^{7}Li spectrum of a mixture of *t*-butyllithium and alkenyllithium in cyclopentane: dotted curve, calculated for the same total concentration before mixing. Scale as in Figure 3.

much of the original *t*-butyllithium remains and only exchanges slowly with the rest. The equilibrium distribution of the species must be quite asymmetric and biased toward undissociated *t*-butyllithium tetramers. The same situation was observed in benzene, the spectrum being identical within the limits of experimental error.

It can be confirmed by viscosity measurements in hexane that *t*-butyllithium does not exchange as completely with polyisoprenyllithium as does *sec*-butyllithium. The concentration range in this case is of course much lower. A drop in dilute solution viscosity (η_{sp}/C) to 70% of its original value is caused by adding a fourfold excess of *sec*-butyllithium to polyisoprenyllithium. The same decrease requires an eightfold excess of *t*-butyllithium. Once again the viscosity reaches its limiting value within the time required for measuring the flow (~10 min) and does not change thereafter. Since in the viscosity experiments the molecular weight of the polyisoprenyl chain was much greater than used in the nmr experiments and hence much greater than that of the butyl group, any mixing of the separate species must cause a drop in average molecular weight and hence in dilute solution viscosity.

Conclusions

Most of the systems studied, *i.e.*, those not involving *t*-butyllithium, show fast exchange in cyclopentane at room temperature. The time scale between intermolecular exchange events must be fractional seconds. Under polymerization conditions in aliphatic solvents, where initiation takes many minutes, one may presume that when initiator is still present, a moving equilibrium distribution of alkyl and alkenyl species should be maintained. The exception seems to be the *t*-butyl containing systems, where complete intermolecular exchange takes many hours in mixing with either lithiomethyltrimethylsilane or *sec*-butyllithium. The alkenyl/*t*-butyl system behaves somewhat differently for an asymmetric equilibrium distribution is formed within the few minutes required for mixing and examination. It was suggested by Brown that the slow exchange of *t*-butyl-containing systems was determined by a slow dissociation rate of *t*-butyllithium aggregates. This explanation could be valid for the mixtures with *sec*-butyllithium and lithiotrimethylsilane where mixing seems to require approximately the same period of several hours. It cannot hold, however, for the *t*-butyllithium/polyisoprenyllithium system, since the dissociation hypothesis would require equilibration again to require several hours, whereas the time scale is no greater than minutes. It would seem that a different intermolecular exchange process occurs when polymer species are involved which might involve direct attack as previously suggested.[5] There is no doubt that exchange with *t*-butyl-containing species is slower than with either *n*-, *sec*-butyl or silyl compounds and mixing is less random when it occurs. This suggests that under some conditions use of *t*-butyllithium as a polymerization initiator could lead to different kinetic behavior than has been observed previously with the other initiators. This phenomenon has in fact been observed both in the polymerization of styrene and isoprene.[10]

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Polymerization of α-*n*-Alkylstyrenes. I. Preparation of the α-*n*-Alkylstyrenes

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ABSTRACT: The Wittig reaction was used to prepare a series of new, pure, isomer-free α-*n*-alkylstyrenes. α-Pentyl-, α-heptyl-, α-nonyl-, α-undecyl-, α-tridecyl-, α-pentadecyl-, and α-heptadecylstyrene were prepared in 50–68% yields. To date, no pure, isomer-free α-*n*-alkylstyrene (alkyl > C_2H_5) has been reported. The identity of the new compounds was established by infrared spectroscopy and elemental analysis, and their homogeneity was proven by gas–liquid partition chromatography. As a preliminary experiment, the homopolymerization behavior of α-heptylstyrene and α-nonylstyrene were studied using sodium naphthalene as the catalyst at $-75°$. Both compounds formed low molecular weight polymers after 72 hr. The experimental evidence indicates that if an α-*n*-alkylstyrene is devoid of isomers, steric hindrance will not prevent homopolymerization.

In the course of the study on polymers having long alkyl chains, experiments were undertaken on the preparation of α-alkylstyrenes and steric and alkyl group length effects on polymerization. Aside from α-methylstyrene, there is very little information in the literature concerning the preparation and polymerization of α-alkylstyrenes.

Overberger, *et al.*,[1] suggested that the reason α-ethylstyrene forms only dimers and trimers under the same conditions (cationic polymerization) that α-methylstyrene forms a high molecular weight polymer is steric factors associated with the ethyl group. The

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