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Star-Branched Polymers. 2. The Reaction of Dienyllithium Chains with the Isomers of Divinylbenzene

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ABSTRACT: The crossover and subsequent homopolymerization reactions of *m*- and *p*-divinylbenzene with butadienyl- and isoprenyllithium in benzene have been followed by UV spectroscopy. The *p*-divinylbenzene was found to react slightly faster with the dienyllithium chain ends than the meta isomer. Nonetheless, *m*-divinylbenzene was found to be more effective than the para form in linking the dienyllithium chains into the star-branched architecture, i.e., at a given DVB/RLi ratio the meta isomer yielded a higher extent of branching than did the para form.

Star-branched polystyrene–polydiene block copolymers and polyisoprene homopolymers containing up to 56 weight-average number of arms have been synthesized[2-5] using divinylbenzene as the linking agent. This procedure involved the addition of the divinylbenzene to the solution of polydienyllithium chains after the diene monomer has been consumed. Thus, the polymerization of divinylbenzene formed the microgel nucleus of these star-shaped polymers, a procedure adumbrated by Milkovich in 1965.[6] Rempp and co-workers[7-12] were the first to successfully exploit this concept, in this case with regard to the synthesis of star-branched polystyrenes. The arms of these star species possessed narrow molecular weight distributions as a result of the termination free aspect[13] of diene and styrene polymerizations initiated by organolithium species in hydrocarbon solvents.

An examination of the rheological properties of these star-branched block and homopolymers[2,4] in the melt state has shown that viscosity is *independent* of the extent of branching and depends only on arm molecular weight. In view of this, and the interesting and unexpected dilute solution properties and chain dimensions of these star-shaped polymers,[4,5] it was deemed of interest to investigate the star formation process involving the reaction between the dienyllithium chain ends and the divinylbenzene isomers. The formation of a star polymer by the reaction of divinylbenzene would be anticipated to be kinetically and mechanistically a complex reaction requiring the participation of several simultaneous and competitive steps. This process was followed by UV spectroscopy using benzene as the solvent and oligomeric dienyllithium chains.

Experimental Section

These anionic polymerizations involved the purification prior to use of monomers, solvent, the divinylbenzene isomers and all glassware equipment. All purifications and polymerizations were conducted under high vacuum (10^{-6} Torr) using the procedures described elsewhere.[2,14] The initiator was *sec*-butyllithium which was purified by distillation under vacuum conditions. The resulting benzene solutions of the initiator were colorless.

The *m*-, *p*-divinylbenzene mixture was obtained from Chemical Samples. The analysis (as outlined below) of this mixture showed that it was 93% divinylbenzene with a meta–para ratio of 3/1. The major impurities were the ethylvinylbenzene isomers. The *m*-divinylbenzene was obtained from Haven Chemical while the para isomer was separated from a commercial mixture (Foster-Grant 80% divinylbenzene) by the complexation with cuprous chloride[15-18] at 0 °C followed by heating. The *p*-divinylbenzene was then further purified by crystallization from methanol. Worsfold[9,19] has also used this separation technique successfully. For run 28a the para isomer was obtained from the meta and para mixture from Chemical Samples. Analysis of the two isomers by IR, 300 MHz ^{1}H NMR, ^{13}C NMR, gas chromatography, and mass chromatography showed that each isomer was >95% pure. The major impurity in each species was the other isomer with only trace amounts of the ethylvinylbenzene species present. Following purification, the divinylbenzene isomers were diluted with benzene to give 5–10% (v/v) solutions. These were stored in ampules under high vacuum at −20 °C until use. Out experience has shown that divinylbenzene solutions of this concentration can be stored at this temperature for at least 1 year without the loss of vinyl groups through dimerization or polymerization.

The poly(dienyl)lithium chains were made by reacting a dilute monomer–benzene solution with *sec*-butyllithium. Reaction periods of 72 to 96 h at room temperature were used in order to ensure that no diene remained. These solutions were cooled several times in order to draw into solution residual diene existing in the void volume of the reactor. These reaction mixtures were then divided into ampules and stored at −20 °C until use. Parenthetically, it should be noted that NMR and UV analysis by numerous workers has shown that these dienyllithium chain ends undergo no transformations, e.g., isomerization or lithium hydride elimination, under the conditions used in this work for their preparation. Thus, in hydrocarbon solvents these allylic lithium species exhibit the degree of stability necessary for general mechanistic evaluations. This is not the case for the allylic sodium or potassium species[20,21] or for the "dicarbanionic tetramer" of α-methylstyrene involving either of these two counterions. This initiator has been shown to be unstable,[22-24] particularly under the influence of white light and UV radiant energy.[24]

The UV spectroscopic measurements were carried out at 21

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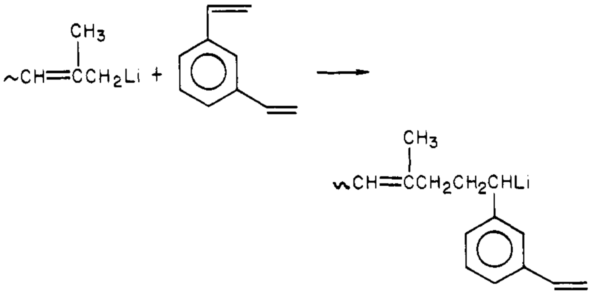
°C using a Perkin-Elmer 450 spectrometer. Both 1 mm and 1 cm path length quartz cells were used. The extinction coefficients were determined to be 0.95×10^4 for *m*-vinylbenzyllithium and 1.65×10^4 for the para isomer at the wavelengths of 390 and 395 nm, respectively.

Following the spectroscopic analysis the solutions were terminated by the addition of degassed methanol. Termination by exposure to the atmosphere was not done since this can lead to some chain coupling.[25] The polymer was then isolated and dried. Characterization was carried out using both membrane osmometry and gel permeation chromatography (GPC). The Hewlett-Packard 503 osmometer was used with a 600D membrane and toluene at 37 °C. The instrument was checked by the use of several solutions of polystyrene standards. The values of $\bar{M}_n$ were determined from measurements made on solutions of at least four concentrations in conjunction with the typical $(\pi/c)^{1/2}$ vs. concentration plot procedure. The gel permeation chromatography analysis was accomplished using the Waters Ana-Prep instrument equipped with the usual refractive index detector. The carrier solvent was tetrahydrofuran at 35 °C. The column arrangement consisted of seven 4-ft columns with a continuous porosity range of 10^3 to 10^6 Å. The columns were calibrated with low molecular weight polydienes synthesized and characterized in these laboratories. The plate count of this seven-column set was 940 plates/foot at a flow rate of 1 mL min^{-1}. Previous work[26,27] has shown that this seven-column set can yield both $\bar{M}_n$ and $\bar{M}_w$ values for a series of polystyrenes which are in close (±5%) agreement with the values determined by absolute measurements. Full loop (2 mL) injections were used while solution concentrations ranged from $^1/_8$ to $^1/_4$% (w/v).

Results and Discussion

Two isomers of divinylbenzene are of practical importance: the meta and the para. Many previous polymerization studies using divinylbenzene have been conducted with material which was not only a mixture of these isomers, but which also contained substantial proportions of the three vinylethylbenzenes. Notable exceptions are the work of Rempp[11,12] and Worsfold.[9,19] The present study also employed pure single isomers of divinylbenzene.

The initial product of the reaction of poly(isoprenyl)-lithium with *m*-divinylbenzene was the vinylbenzyl anion (reaction 1) which has absorption maxima at 316 and 390 nm (Figure 1a). *Shortly* after the first appearance of this species, the concurrent formation of the metal alkylbenzyl ion (λ_{max} 335 nm) commenced (reaction 2). The overlap of these bands generated a broad absorption envelope (Figure 1a,b) which increased in intensity with time. In the final stage of reaction, Figure 1c, the alkylbenzyl absorption intensified at the expense of the vinylbenzyl absorbance with successive spectra passing through an isosbestic point near 365 nm. It is clear that this was due to reaction 3. It seems most probable that the inter-



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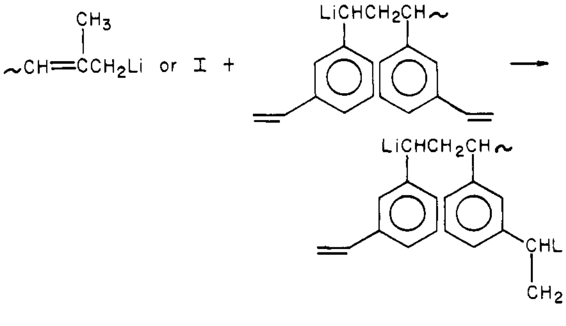

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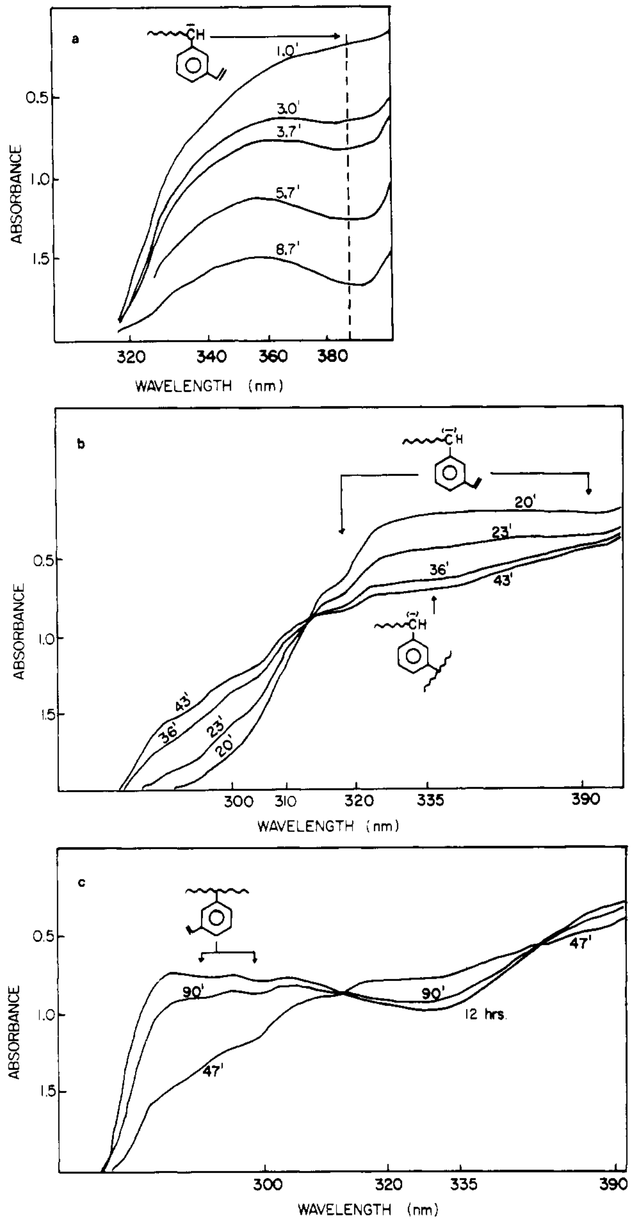
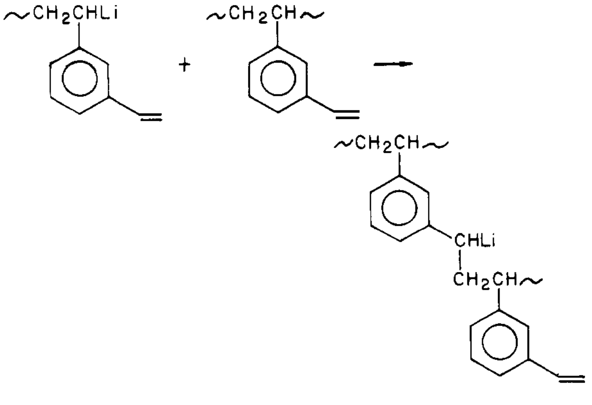


Figure 1. Spectra of *m*-divinylbenzene–isoprenyllithium: run 8.



(3)

mediate phase in which the concentrations of vinylbenzyl and alkylbenzyl ions have increased corresponds to the simultaneous occurrence of reaction 1 and reaction 2 wherein either the allyl or vinylbenzyl chain end reacts with the vinyl group of an in-chain, nonterminal, divinylbenzene residue.

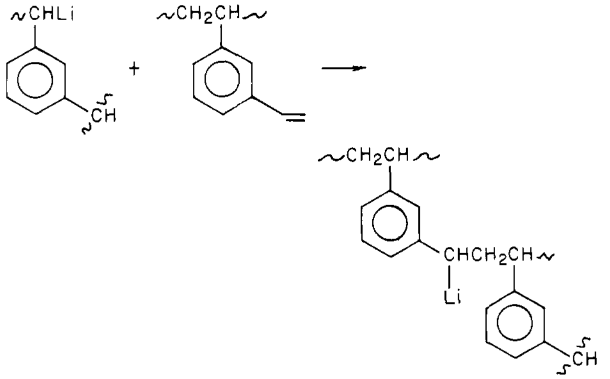
Table I
Rate Data for the Reaction of Dienyllithium Chains with the Isomers of Divinylbenzene

sample[a]	DVB isomer	$10^3 \times$ DVB mol dm^{-3}	$10^3 \times$ RLi mol dm^{-3}	$10^5 \times$ initial rate, R, mol dm^{-3} min^{-1}	$R/\{[\mathrm{RLi}]^{1/2} \times [\mathrm{DVB}]\}$
3	m, p	8.26	1.16	4.5[b]	0.16
4	m, p	8.59	1.15	3.2[b]	0.11
5	m	5.55	1.16	2.6	0.14
6	m	7.45	1.14	6.7	0.27
7	m	7.82	0.94	3.0	0.13
8	m	7.23	0.95	2.3	0.11
10	m	10.6	0.92	3.3	0.10
11	m	6.83	0.95	2.6	0.12
12	m	3.38	0.99	1.8	0.17
13	m	8.77	1.03	4.0	0.14
14	m	7.79	1.05	3.2	0.13
15	m	9.80	1.03	4.2	0.13
16	m	3.29	1.10	2.0	0.18
18	p	8.19	1.40	6.1	0.20
19	p	9.47	1.01	8.7	0.29
20	p	4.87	1.45	3.2	0.17
21	p	3.95	0.58	1.9	0.20
22	p	8.22	0.68	3.9	0.18
23	p	4.07	0.87	2.5	0.21
25	m	11.3	1.35	0.11	2.7×10^{-3}
26	m	17.2	1.28	0.18	2.9×10^{-3}
27	p	11.4	1.34	0.36	8.6×10^{-4}
28	p	5.77	1.41	*c*	
28a	p	6.02	1.40	*c*	
29	m	4.65	1.43	0.030	1.7×10^{-3}
30	m	7.25	1.39	0.039	1.4×10^{-3}
31	m	10.1	2.50	10.0	0.20
32	m	4.38	2.66	3.7	0.17
33	m	6.90	0.77	4.2	0.22
34	m	3.88	0.69	2.5	0.25

[a] Samples 3-23 and 31-34 were isoprenyllithium and 25-30 were butadienyllithium. [b] Since the predominant isomer was the meta form, the extinction coefficient for *m*-divinylbenzene was used in the calculations. [c] No rate could be assigned as the reaction was markedly autocatalytic.

The *initial* rate of formation of the vinylbenzyl ion was determined for a series of experiments and the results are summarized in Table I. Because of the need to measure the rate immediately after mixing in order to minimize perturbation by competing processes, *individual measurements are subject to significant errors.* There seems little doubt that the reaction is first order in divinylbenzene. The range of concentration of organolithium studied was insufficient to test the order in this species. Also, the scatter in the data precluded a legitimate estimate of the reaction order. Thus, the apparent rate constant (Table I) for the crossover reaction has been calculated on the *presumption* that the order is one-half. We have calculated the data in this fashion merely to provide insight into the relative magnitudes of the apparent crossover rate constants. Our presentation of the data in this fashion cannot, and should not, be taken as a demonstration or claim of a one-half dependency of the crossover rate on chain end concentration. It is well known that reactions (additions to double bonds and metallations) involving organolithium species can exhibit a variety of reaction orders[14] ranging from about $^1/_6$ to 1.4 in hydrocarbon solvents.

At the onset of the final stage of reaction, about 95% of the original allylic lithium was present as alkylbenzyllithium and 5% as vinylbenzyllithium. As this residual vinylbenzyl ion was converted to the alkylbenzyl species, the absorption bands of the in-chain styrenoid residues at 287 and 297 nm decreased in intensity considerably more than expected for the participation of reaction 2 alone. This indicated that the residual vinyl groups were also being attacked by the alkylbenzyl ion (reaction 4). In accord with the near-constant concentration of benzyl ion, the disappearance of the absorption band at 297 nm was found to obey pseudo-first-order kinetics. Assuming a half-order dependence on alkylbenzyl ion concentration, a mean rate constant of 0.62 mol$^{-1/2}$ dm$^{3/2}$ min^{-1} was found, a value similar to that found[28] for the propagation of poly(styryl)lithium in benzene, viz., 0.65 at 30 °C. Generally it was observed that after 24–48 h the residual concentration of vinyl groups from the meta isomer was about 10–15% of the initial value while about 20–25% remained from the para isomer.



(4)

Qualitatively, the crossover reaction of poly(isoprenyl)lithium with *p*-divinylbenzene was similar to that with the meta isomer. The formation of the *p*-vinylbenzyl ion by the analogue of reaction 1 was accompanied by the development of an absorption band at 390 nm. The formation of significant quantities of *p*-alkylbenzyl ion was slow in comparison with the *m*-divinylbenzene. Under the conditions used it was estimated that vinylbenzyllithium representing as much as perhaps 30% of the initial chain ends was still present even after 24 h. This reluctance to convert to the alkylbenzyl ion is probably due to the significant loss of resonance stabilization incurred—much larger, for example, than that involved with the meta isomer. The reluctance of this residual *p*-vinyl group to react in anionic polymerizations has also been reported by Worsfold.[19,29] It should also be noted that *the initial rate* of formation of the *p*-vinylbenzyl ion from isoprenyllithium was found (Table I) to be about twice that observed for the corresponding reaction of the meta isomer.

The formation of the vinylbenzyl ion by *m*-divinylbenzene and poly(butadienyl)lithium was an unexpectedly slow process (Table I); the conversion to the alkylbenzyl ion was also slow, but relatively less so than in the polyisoprene case. The reaction was otherwise unremarkable.

The system poly(butadienyl)lithium–*p*-divinylbenzene was a particularly interesting one because of its unusual kinetic behavior. The most obvious feature (Figure 2) was that although the formation of vinylbenzyl ion was initially exceedingly slow, the rate increased markedly with time. Such behavior is reminiscent of autocatalysis in which a reaction product catalyses the reaction from which it was formed. The autocatalytic behavior could be accounted for if the dimeric cross-associate (–CH=CHCH$_2$Li:LiC-

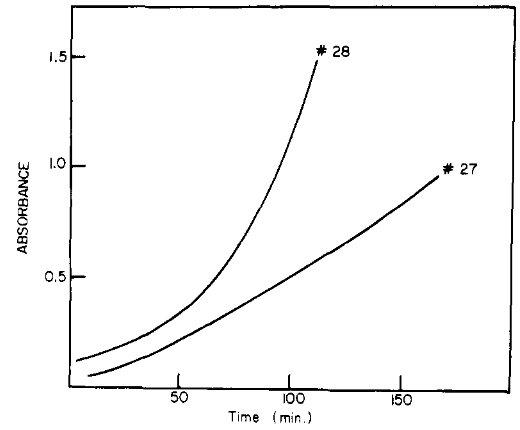


Figure 2. Appearance of the vinylbenzyl ion in runs 27 and 28 as a function of time. Run 28a was indistinguishable from run 28.

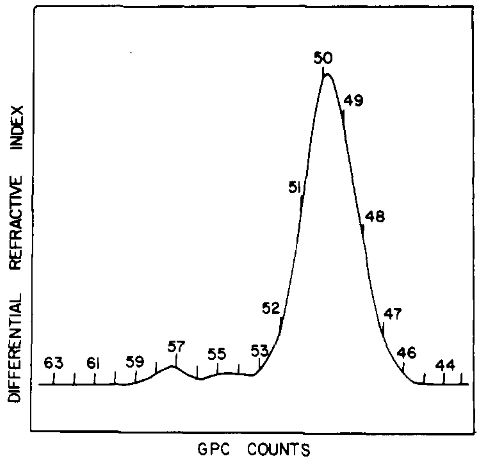


Figure 3. Chromatogram of polybutadiene star 27.

$H_2(C_6H_6)$–) were much more reactive toward divinylbenzene than the dimer of poly(butadienyl)lithium itself (the dimeric state of association for styryl and allylic lithium chain ends has been established[30–35] by viscosity, light scattering, and cryoscopic measurements.) Acceleration has also been noted[36,37] in the reaction of *sec*- and *tert*-butyllithium with isoprene and styrene in cyclohexane (although not in benzene) which could similarly be rationalized in terms of cross-associates of enhanced reactivity. The increased interionic separation in an ion pair occasioned by cross-association has been observed in the system *n*-butyllithium–1,3-diphenylbutenyllithium in the poorly solvating media dioxane and diethyl ether.[38] An increase in interionic separation seems invariably to increase the reactivity in addition across double bonds.[39]

Comparison of the spectra of experiments 27 and 28 is interesting for another reason than the autocatalytic behavior. The concentrations of poly(butadienyl)lithium were almost identical. However, although the concentration of *p*-divinylbenzene was only half as much in runs 28 and 28a as it was in 27, it paradoxically was the former runs which exhibited the more rapid development of absorbance due to the vinylbenzyl ion (Figure 2). The obvious interpretation that some termination of the chain ends by adventitious impurities occurred in 27 is refuted by the GPC chromatogram which shows no trace of material derived from unlinked parent (Figure 3). The small fraction of low molecular weight material eluting at count 57 corresponds approximately to a tetramer of the parent which was independently shown to have a peak elution count of 61.5.

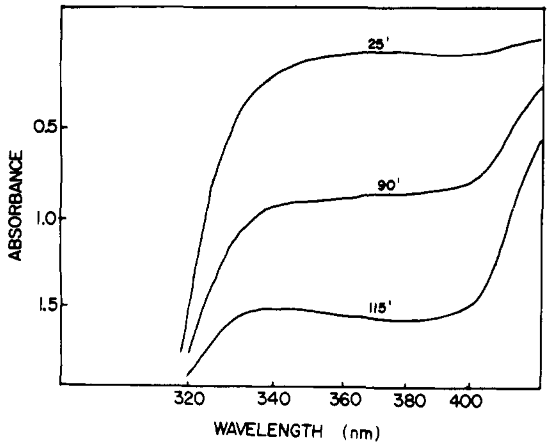


Figure 4. Spectra of *p*-divinylbenzene–butadienyllithium run 28.

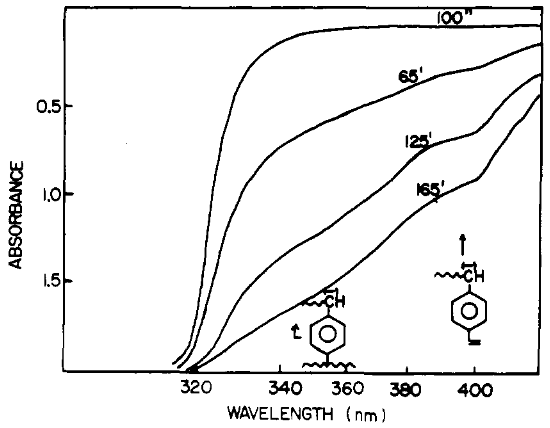
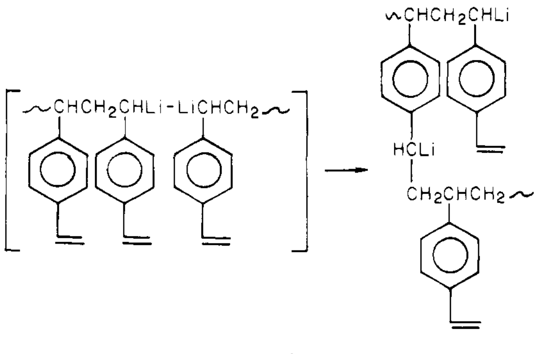


Figure 5. Spectra of *p*-divinylbenzene–butadienyllithium: run 27.

A possible rationalization may be as follows. In run 28 (Figure 4) the alkylbenzyl and vinylbenzyl ion absorbances increased at very similar rates whereas in 27 (Figure 5) the alkylbenzyl band grew much more rapidly than that due to the vinylbenzyl species. Since the divinylbenzene concentration is higher in 27, there must have been more rapid propagation of polymerization of the *p*-divinylbenzene.

As soon as two or more divinylbenzene residues become attached to a polybutadiene chain, reaction between the vinylbenzyl ion and an in-chain neutral residue becomes possible (reaction 5). This reaction is, accordingly, in more



(5)

effective competition with the formation of the vinylbenzyl ion in run 27 than in 28, with the consequent reduced net rate of formation of vinylbenzyl ion. The occurrence of such an "incestuous" process within a dimeric associate is, of course, equally probable when the original parent is poly(isoprenyl)lithium. However, the intrinsically

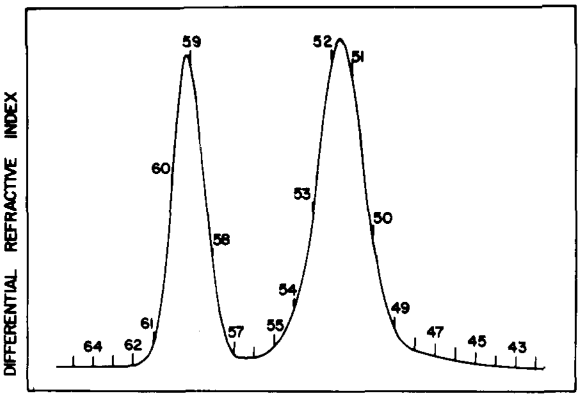


Figure 6. Chromatogram of polybutadiene star 28.

greater reactivity of the latter compared to poly(butadienyl)lithium indicates that reaction 2 plays a dominating role. In addition to the conversion of the *p*-vinylbenzyl ion to the alkylbenzyl ion there is also the probability of reaction 3 (more properly written as a reaction involving *two* dimeric aggregates). Parenthetically, it should be noted that no spectroscopic evidence for the formation of the xylylene dianion from either isomer was found in this work. This species would be expected to be infrequently formed as a result of the fact that energetically the formation of the xylylene dianion would be improbable in hydrocarbon solvents.

Examination of the GPC trace of reaction 28 (Figure 6) shows that it is strikingly bimodal. What is especially interesting is that the lower molecular weight fraction eluted at count 59.1. Comparison with the parent, which eluted at a count of 61.5, shows that this fraction is predominantly dimer. Such a preference for dimer formation can be accounted for by invoking the intradimer conversion of the vinylbenzyl ion to the alkylbenzyl ion as a significant process in competition with reaction 3. A similar chromatogram was obtained for the product of run 28a.

If all limitations imposed by polarity, steric, and mechanistic requirements (e.g., chain end "self"-association and cross-association) are ignored, it is clear that j molecules of divinylbenzene could, in priciple, link together $(j + 1)$ polymer chains. That the extent of linking is much smaller can be seen in Table II. These results show that the effect of these neglected parameters is profound. It is not difficult to see how requirements of polarity may enter if we consider a simple model in which three dienyl anions react with three divinylbenzene molecules. Three situations can be envisaged (Table III). From electrostatic considerations, the liklihood of attack by a vinylbenzyl anion upon the (formal) vinyl group of an identical ion is very slight. Thus situation (1) is most unlikely to lead to rapid linking. In situation (2), however, the neutral in-chain divinylbenzene residue is expected to be susceptible to attack by the vinylbenzyl ion or, more readily, by the allyl chain end, resulting in the linking of two of the three chains. Finally, it is clear that all three chains can be easily linked starting from situation (3). In a real situation, self- and cross-association may well complicate the issue, but it is clear from this simple example that the extent of linking can be retarded by (a) increasing the rate of the crossover from dienyl to vinylbenzyl ion and by (b) reducing the homopropagation rate of the divinylbenzene.

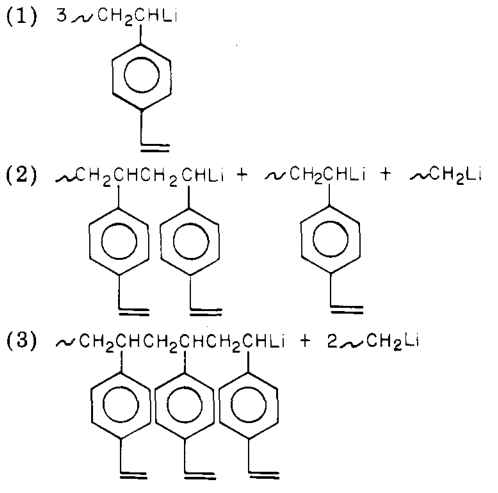
An additional comment on the mechanism of star-branched polymer formation can be made based on a series of polydienes which were linked with the two divinylbenzene isomers. Aliquots of the reaction mixture were terminated over a period of time during the linking reaction. The chromatograms showed that the peak elution volume of the branched fraction *decreased* with increasing reaction time. This is a result of the increasing molecular weight of the branched fraction in these star materials which manifests itself by a decreased residence time in the GPC columns.

Table II
Number-Average and GPC Characterization of Polydiene Stars Linked in Kinetic Studies

sample[a]	$M_n \times 10^{-4}$ [b] g mol^{-1}	wt % star	wt% linear	N[c]	V_R[d] GPC	DVB isomer	DVB/ RLi
PI-2	3.8_0	$95._7$	$4._3$	11	52.0	m, p	5.8
-3	2.6_3	$90._4$	$9._6$	10	51.8	m, p	7.1
-4	2.7_4	$93._9$	$6._1$	8	52.4	m, p	7.4
-5	1.9_4	$84._7$	$15._3$	8	52.3	m	4.8
-6	2.9_0	$93._5$	$6._5$	9	52.1	m	6.5
-8	3.4_0	$91._0$	$9._0$	16	51.3	m	7.5
-10	3.3_0	$90._0$	$10._0$	17	51.1	m	11.5
-11	3.5_5	$91._0$	$9._0$	18	51.4	m	6.7
-12	2.6_2	$88._9$	$11._1$	11	52.9	m	3.4
-14	4.1_0	$91._4$	$8._6$	19	51.1	m	7.4
-15	4.3_0	$91._5$	$8._5$	21	51.0	m	9.5
-16	2.9_5	$90._8$	$9._2$	10	51.8	m	3.0
-18	3.4_0	$93._1$	$6._9$	10	51.9	p	5.9
-19	5.7_7	$98._0$	$2._0$	13	51.5	p	9.3
-20	1.7_7	$73._8$	$26._2$	15	52.3	p	3.3
-21	5.0_7	$93._9$	$6._1$	20	51.2	p	6.8
-22	4.3_4	$95._6$	$4._4$	12	51.4	p	12.0
PBd-25[e]	2.8_1	$91._3$	$8._7$	24	51.2	m	8.3
-26[e]	2.8_8	$91._2$	$8._8$	27	50.8	m	13.4
-27[f]	7.7_0	$97._1$	$2._9$	39	49.8	p	8.4
-28[e]	1.1_1	$62._0$	$38._0$	18	51.6	p	4.1
-29[e]	1.5_8	$82._3$	$17._7$	16	51.8	m	3.2

[a] Arm $\overline{M}_n$ values: samples 2-6, $\overline{M}_n = 4.9 \times 10^3$; 8-12, $\overline{M}_n = 5.0 \times 10^3$; 14-16, 19, $\overline{M}_n = 5.5 \times 10^3$; 18, 20-22, $\overline{M}_n = 5.5 \times 10^3$; 25-29, $\overline{M}_n = 2.5 \times 10^3$. [b] These values represent the star molecular weights. They were obtained by correcting the measured values for the unlinked parent chains present. [c] N = number-average of arms; this value is derived from the corrected M_n values for the star-linear mixtures. [d] V_R is the peak elution volume (in 5 mL counts) of the chromatograms. [e] The $\overline{M}_n$ of the low molecular weight component was determined from the GPC measurements. [f] No linear material present. The lowest molecular weight component seemed to be a four-armed star.

Table III
Products from the Reactions of Three Dienyllithium Chains with Three *p*-Divinylbenzene Molecules[a]



[a] In the interest of simplicity aggregation is not represented.

These results show that the extent of branching for these star-shaped materials *increases* with reaction time and that the maximum extent of branching is not reached until the later stages of the reaction. In other words, the star formation process involves, at least in part, the addition of unlinked (or perhaps coupled) parent material to branched polymer. These observations are in accord with the divinylbenzene linking reaction characteristics discussed previously.

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Interactions of Small Ions with Heparin and Dextran Sulfate by Self-Diffusion Measurements

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ABSTRACT: Self-diffusion coefficients for Na^+, Ca^{2+}, Cl^-, and SO_4^{2-} were determined in aqueous solutions of sodium heparin and sodium dextran sulfate at 25 °C. Simple salt concentrations of 0.00050, 0.0010, 0.0050, and 0.010 N were used and the equivalent concentrations of the ionic polysaccharides were in the range of 0.000050 to 0.10 N. The sodium ion diffusion coefficients were found to decrease initially as X increased from zero to approximately six, X being the ratio of the equivalent concentration of ionic polysaccharide to the molar concentration of simple salt, followed by a leveling off as X increased. The calcium ion diffusion coefficients showed a greater initial decrease at low X values prior to its leveling off than did the values for sodium ions. For both ionic polysaccharides, the diffusion coefficients for Cl^- ion were close in value to those for SO_4^{2-} ion at corresponding X values. The experimentally obtained diffusion coefficients are correlated with those predicted from the Manning theory of polyelectrolyte solutions.

Ionic polysaccharides are of paramount importance because of their roles in biological phenomena. Their importance in the chemistry of connective tissue, of the eye, and of blood is evidenced by the growing number of publications in the field. A principal aspect of elucidating the behavior of ionic polysaccharides is a study of the interactions of small ions with these biological polyelectrolytes in aqueous salt solutions. Biological systems involving polyelectrolytes could be better understood with the aid of a good model and the model could act as a guide to further studies. The Manning theory[1-6] has proven most useful in our research endeavors because of its success in describing both transport and equilibrium properties.

Counterions and coion interactions with polyelectrolytes in aqueous salt solutions have been investigated by determining the tracer diffusion cofficients of the desired small ion. From studies on such polyelectrolytes as sodium poly(styrene sulfonate),[7] sodium polyacrylate,[8,9] sodium, calcium, strontium chondroitin sulfate,[10,11] sodium carboxymethylcellulose,[12] sodium alginate,[13] and sodium ι-

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