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Studies on Dilithium Initiators. 2. The Bimodal Molecular Weight Distribution in Polyisoprene

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ABSTRACT: The development of bimodal molecular weight distribution in polyisoprene was studied by GPC analysis of samples taken during the polymerizations initiated by the dilithium initiators reported in paper 1 of this series. Isolation of the individual peaks using selective precipitation techniques was applied on several samples to identify the nature of the peaks in GPC chromatograms. The dilithium initiators were found to react quickly with isoprene monomer to form an adduct. Further polymerization from the adduct was very slow and caused the main peak of the distribution to be slightly broader and lower in molecular weight. The higher molecular weight peak of the bimodal distribution was from the inadvertently present monofunctional initiation. The major source of the monofunctional initiating species was identified to be the dilithium initiator partially terminated by the residual impurities in the polymerization feed.

Introduction

In an earlier paper,[1] hydrocarbon-soluble dilithium initiators 1,3-phenylenebis(3-methyl-1-phenylpentylidene)-dilithium and 1,3-phenylenebis[3-methyl-1-(methylphenyl)pentylidene]dilithium were reported. These dilithium initiators were prepared from the stoichiometric reaction of *sec*-butyllithium (s-BuLi) with 1,3-bis(1-phenylethenyl)benzene (PEB) or 1,3-bis[1-(methylphenyl)ethenyl]benzene (MPEB) in hydrocarbon solvents, and the reaction mixtures were used directly for anionic polymerization. Styrene–butadiene–styrene (SBS) triblock copolymers of good tensile properties were prepared by using these dilithium initiators. However, the polymerization had some unusual characteristics. The SBS prepared, though of good tensile strength, had a molecular weight distribution broader than that expected from normal living anionic polymerization, and the distribution was also sensitive to minor uncontrollable variations of polymerization conditions. Broske et al.[2] reported narrow monomodal distribution polybutadiene from the PEB-based initiator when samples were taken before the completion of the polymerization, but the distribution of the final polybutadiene was broad. Bastelberger and Höcker[3] obtained polybutadienes with broad bimodal distributions using another dilithium initiator of a much lower solubility than the initiators based on PEB or MPEB. They attributed the high molecular weight peak in the bimodal distribution to the 35% monofunctional initiating species estimated to be in their initiator system. Quirk and Ma[4] obtained a bimodal distribution for low molecular weight polybutadiene using the initiator based on PEB. Because of their high-vacuum techniques and rigorous purification procedures, they did not believe that the high molecular weight peak in the distribution was monofunctional and attributed the bimodal distribution as the result of the kinetic characteristics of dilithium initiation.

The bimodal distribution appeared to be more evident in isoprene polymerization. When the initiator based on PEB was used to make styrene–isoprene–styrene (SIS) triblock copolymers, low tensile strength samples were obtained and the molecular weight distribution of the samples were distinctly bimodal.[1] Significant improvement of SIS properties was achieved only when polar additives,[1,5] or seeding,[5] were used. Investigation on these unusual characteristics in dilithium initiated polymerizations is presented in this paper. Isoprene polymerization was studied because the bimodal distribution appeared to be more pronounced in polyisoprene samples.

Results and Discussion

Development of the Bimodal Molecular Weight Distribution. To follow the development of the bimodal distribution, an isoprene polymerization was conducted in cyclohexane using a PEB-based initiator. In the preparation of the initiator, the reaction products were monitored by gas chromatography (GC) in order to achieve precise stoichiometric control of the addition of s-BuLi to PEB. A final amount of s-BuLi was added to compensate for any unreacted PEB indicated by the GC analysis. The final concentration of the initiator was 0.06 M as determined by the double titration method of Gilman.[6] In the polymerization solution, the isoprene concentration was 1.5 mol/L and the initiator concentration was 0.001 mol/L (at 100% conversion, the polymer solids should be 13.7% and the M_n should be 93 000). The jacket temperature of the reactor was set at 55 °C. About 25 min following initiation, the reaction temperature rose above the jacket temperature to a maximum of 70 °C. At about 40 min, the jacket temperature was reset to 65 °C in order to keep the polymerization at a rapid rate. Samples were taken at various times from a discharge port at the bottom of the reactor and terminated by 2-propanol for GPC analysis and for the determination of percent monomer reacted (conversion).

The development of the bimodal distribution is shown in Figure 1 by the GPC chromatograms of samples taken during the course of the polymerization. The traces in the chromatograms were recorded from both a differential refractive index detector (RI, lower curve) most sensitive to polyisoprene and a UV detector (upper curve) sensitive only to the aromatic initiator. The terminated initiator in Figure 1a was marked with a peak molecular weight of 441. This is the molecular weight based on an extrapolation of the GPC polystyrene calibration curve. The formula weight of the terminated dilithium initiator is 398. The first sample taken at 4.3% conversion in Figure 1b showed two sharp peaks in its chromatogram. Peak B,

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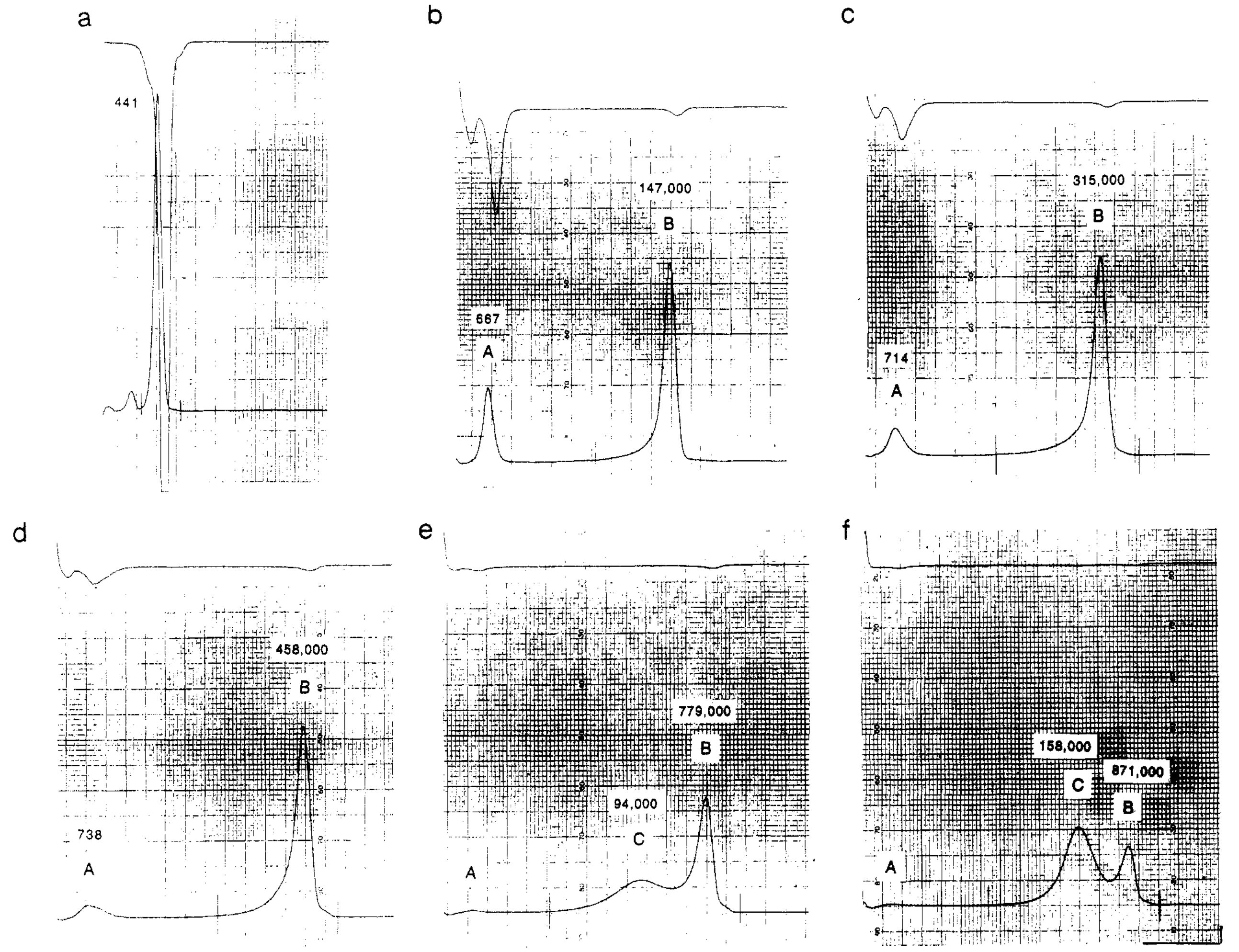


Figure 1. GPC chromatograms of samples from isoprene polymerization run 1 initiated by a dilithium initiator based on PEB. Min is the time when the sample was taken; % is the monomer conversion. The upper curve is the chromatogram from the UV detector, and the lower curve is from the differential refractive index detector. (a) Terminated initiator. (b) 5 min, 4.3%. (c) 10 min, 8.1%. (d) 15 min, 13.2%. (e) 30 min, 47.4%. (f) 70 min, 95.3%.

at a molecular weight of 147 000 (polyisoprene scale), should be a polyisoprene peak. Peak A is not the same as the terminated initiator peak in Figure 1a because its molecular weight based on the extrapolation of polystyrene calibration is higher. The UV intensity of the peak is relatively smaller in comparison with the terminated initiator, indicating that the peak should be the initiator with a few isoprene units attached. At the 10 min and 8.1% conversion mark (Figure 1c), the two sharp peaks started to skew toward each other. After 30 min into the polymerization, a broader peak, peak C, appeared at the low molecular weight tail side of peak B (Figure 1e). The appearance of peak C coincided in time with the sharp temperature rise of the reaction mixture. This broader peak grew to become the major peak in the bimodal distribution of the final polyisoprene. The progression in the chromatograms created an illusion of the "melting" of peak A to form peak C.

The molecular weight of peak B grew the fastest. Between the 30 and 70 min time interval peak B increased nearly 100 000 in molecular weight (polyisoprene scale), while the broader peak, peak C, increased only about 65 000. The growth in size of peak C therefore must be caused by a large increase of the number of chains in the peak. Peak A was not strictly stationary as indicated by the polystyrene scale molecular weight marked for the peak. At 5 min the marked molecular weight of the peak indicates that about 3–4 units of isoprene were added. At 10 min another one isoprene unit was added and less than one isoprene was added from 10 to 15 min. During this period, peak A diminished in size relative to peak B. Between 5 and 10 min peak B doubled in molecular weight but the ratio of its peak height to the peak height of peak A increased more than 2-fold. The relative heights of the two peaks at the 15-min time show a further reduction of peak A. The number of polymer chains in peak B in chromatograms b–d was roughly constant. The molecular weight of peak B in the chromatograms had an approximate ratio of 1:2:3 and so was the conversion. At the end of the reaction, the weight percent of peak B as determined from the areas of the peaks in the chromatogram was about 27%. By a rough calculation, the mole percent should be at about 6.3 which was approximately the same as the mole percent of peak B in each of the three early chromatograms.

Two distinct polymerization processes apparently took place—a fast initiation followed by fast propagation responsible for the high molecular weight peak of the bimodal distribution and a slower process for the main peak. The chromatogram at 5 min showed that all dilithium initiator had reacted to form a low molecular weight initiator–isoprene adduct. The slow growth of the initiator–isoprene adduct apparently was responsible for the formation of the broader lower molecular weight main peak of the bimodal distribution. The number-average molecular weight of polyisoprene at 95% conversion was 172 000 which is much higher than the 93 000 predicted by the stoichiometric feed composition. This indicated that close to 40% of the initiator–isoprene adduct remained dormant. A faint trace of peak A for the adduct was indeed visible in the chromatogram at 70 min and 95% conversion.

The dilithium initiator solution had an intensive dark red color. When it was added to the isoprene in cyclohexane solution, the color disappeared rapidly to a faint orange–yellow which was a sign that most of the initiation sites reacted quickly with isoprene. The faint orange–yellow, however, persisted throughout the polymerization, giving an indication that in the initiator–isoprene adduct there might exist a small amount of unreacted initiator sites.

Isoprene polymerization initiated by the MPEB-based dilithium initiator showed the same characteristics as the run using the PEB-based initiator.

Isoprene polymerization initiated by the adduct of s-BuLi to 1,1-diphenylethylene, however, produced a symmetrical and narrow distribution polymer. The slow growth of the initiator–isoprene adduct therefore was not a characteristic of the individual initiating sites on the dilithium initiators but the characteristics of propagation from the difunctional initiator–isoprene adduct.

Initiator–Isoprene Adduct. A second isoprene polymerization (run 2) experiment in cyclohexane was carried out to collect low conversion samples in order to isolate the initiator–isoprene adducts and characterize them by NMR spectroscopy. A MPEB-based dilithium initiator was used. The initiator concentration in the feed solution was 0.004 mol/L, and the isoprene concentration was 0.6 mol/L. The initiation and polymerization temperature was about 55 °C. Four samples (1–4), about 200-mL aliquots each, were taken at 2.5, 5, 10, and 20 min times, and each was terminated with acetic acid. The monomer conversions of these samples determined by the measured solid contents were 3.1%, 4.7%, 8.9%, and 19.5%. Similar to the early GPC chromatograms shown in Figure 1b–d, all four samples showed two narrow peaks (A and B).

The low molecular weight peak, peak A, was isolated by a selective solvent fractionation process. The final isolated samples (1A, 2A, 3A, and 4A) when examined by GPC showed that a clean separation was achieved.

Figure 2 shows a pair of ^{1}H NMR spectra. The benzylic proton derived from direct termination of the dilithium initiator is the triplet peaks at 4 ppm shown in the spectrum for the terminated initiator (Figure 2a). This triplet peak disappeared almost completely in the spectrum for sample 1A (Figure 2b). New peaks which appeared between 4.3 and 5.1 ppm in sample 1A are the protons associated with the double bonds of polyisoprene. Table 1 shows a rough estimate of the amount of isoprene in the adduct based on the peak assignments shown in Figure 2.

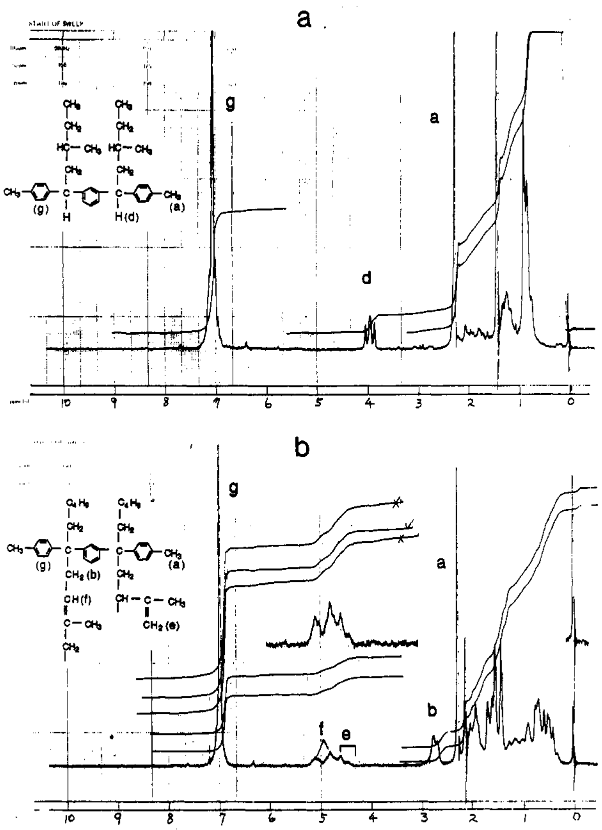


Figure 2. Proton NMR spectra (90 MHz) of the protonated dilithium initiator and the protonated initiator–isoprene adduct. (a) Protonated dilithium initiator based on MPEB. (b) Protonated initiator–isoprene adduct, Sample 1A.

Table 1. ^{1}H NMR Analysis of Samples 1A–4A

sample no.	time (min)	1,4-Isop (%)	3,4-Isop (%)	ave isop units per initiator
1A	2.5	77.4	22.6	3.0
2A	5	79.2	20.8	3.5
3A	10	81.2	18.8	4.0
4A	20	83.3	16.7	5.1

The NMR results are consistent with the concept that peak A was an initiator–isoprene adduct. They show also that the adduct formed rapidly and that isoprene propagation from the adduct proceeded very slowly. Sample 4A shows that in 20 min only 5.1 isoprene units were added to the initiator. The NMR results further revealed that more 3,4 isoprene addition formed during the early addition of isoprene to the initiator. Isoprene units propagated from the adduct were mainly through 1,4 addition.

High Molecular Weight Peak, Peak B. In the above, peak A has been identified to be the initiator–isoprene adduct. The main peak, peak C, is very likely to be the polyisoprene propagated from the adduct represented by peak A as the number of chains in peak C increased with polymerization and that in peak A decreased. The source for the polyisoprene chains in the high molecular weight peak, peak B, remains ambiguous. In isoprene polymerization run 1, described earlier, the dilithium initiator contained about 0.5% monoadduct of s-BuLi with PEB by GC analysis. This monoadduct could be a source for the fast initiating and propagating monofunctional initiator. Peak B, however, was 6 mol % of the total polymer, far exceeding the 0.5% monoadduct. Excess s-BuLi was not likely to coexist with the monoadduct and had been carefully avoided in the procedure for initiator preparation. Other unknown sources of monofunctional initiating species could exist in the polymerization system, but the initiator–isoprene adduct itself could exist in different association states. Isoprene could add readily to one of the association states to form the high molecular weight peak and only very slowly to the other association state to give rise to the broader distribution main peak. The latter view was suggested also by Quirk and Ma[4] to explain the bimodal distribution observed by them in dilithium polymerized polybutadiene.

In order to identify the functionality of peak B, styrene was used to attach a section of polystyrene to the polyisoprene chains to form block copolymers of styrene and isoprene. The high molecular weight peak and the main peak should give block copolymers of vastly different compositions. Their separation by selective precipitation should be easily achieved. If the high molecular weight peak was generated from dilithium initiation, a triblock

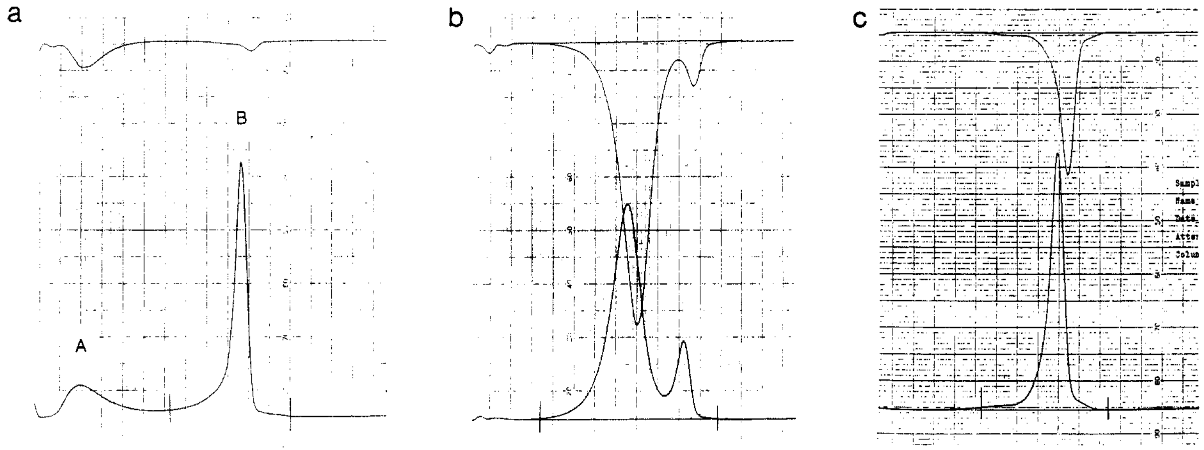


Figure 3. GPC chromatograms of SIS from run 3 prepared by using a dilithium initiator based on PEB. The upper curve is the chromatogram from the UV detector, and the lower curve is from the differential refractive index detector. (a) Polyisoprene before styrene addition. (b) Final SIS. (c) Peak B in b after separation by selective precipitation.

should form upon the addition of styrene and the separated fraction should have a good tensile strength.

Another polymerization experiment (run 3) was made with a PEB-based initiator. The initiator concentration in the polymerization solution was 0.004 mol/L, and the isoprene concentration was 0.3 mol/L. After the completion of isoprene polymerization, styrene monomer was added to the polymerization solution containing the still reactive polyisoprenyl anions. The polyisoprene sample taken before the addition of styrene and the final polymer both gave two distinct peaks as shown by the GPC chromatograms in Figure 3. The low molecular weight peak in Figure 3b had a molecular weight of 38 600 and contained about 98% styrene while the higher molecular weight peak had a molecular weight of 138 000 and contained about 34% styrene.

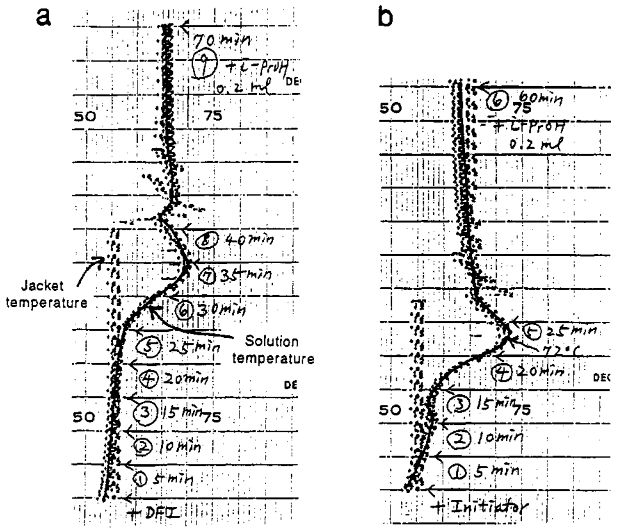
The high molecular weight peak of the final polymer was separated by selective precipitation. The GPC chromatogram (Figure 3c) of the separated high molecular weight polymer gave a composition at 35.6% styrene and 64.4% isoprene as determined by ^{1}H NMR. The dried block copolymer, which should be very strong if it were a triblock, showed no strength. The high molecular weight peak therefore must be derived mainly from monofunctional initiation and had diblock characteristics. The possibility of some triblock mixed with the diblock should be remote because difunctional initiation would have produced another peak with a molecular weight twice as high as that of the monofunctional peak. No such peak was observed. However, Madani et al.[7] reported that the propagation rates of monofunctional and difunctional chains might not be the same. Some difunctional material in the high molecular weight peak therefore cannot be totally ruled out.

Source of Monofunctional Initiation. Polymerization run 3, described above, established that the high molecular weight peak was mainly from monofunctional initiation. To explore the source of monofunctional initiation, four more isoprene polymerization experiments were made.

Isoprene polymerization run 4 was made under the same conditions as run 1 with the exception that the initiator solution was added dropwise until a light yellow tint persisted. The dropwise initiator addition was made to scavenge the residual impurities that might still exist in the polymerization solution after purification. The rest of the initiator solution was then added to start the polymerization. The GPC chromatograms of the samples taken from this polymerization had the same general features as those shown in Figure 1. The amount of the high molecular weight peak, as shown in Figure 4 for the final polyisoprene sample, however, was substantially reduced by virtue of the blanking step in this run. Thus a good portion of the monofunctional initiating species in run 1 must be formed when the dilithium initiator was added all at once. The residual impurities in the feed solution terminated the dilithium initiator partially to monolithium initiator. The high molecular weight peak from monofunctional initiation was estimated to be about 2.6 mol % in this run.

Figure 4. GPC chromatogram of the polyisoprene from run 4 which was prepared with an extra step of blanking of the feed before adding a dilithium initiator.

Isoprene polymerization run 5 was made with a dilithium initiator containing a 9.4 mol % excess of s-BuLi to simulate an increase in the level of monofunctional initiation in the system. All other procedures and conditions were similar to the first isoprene polymerization run. In the other isoprene polymerization, when peak C started to grow, there was an accompanying rise in temperature of the polymerization mixture to 15–20 °C above the set jacket temperature. Such a temperature profile is shown in Figure 5a. The temperature profile of the present run which had 9.4 mol % s-BuLi in the initiator mixture had two exothermic temperature rises as shown



(5a) Run 1: dilithium initiator alone

(5b) Run 5: dilithium initiator with 9.4% s-BuLi

Figure 5. Temperature profiles of two isoprene polymerization runs. (a) Run 1: dilithium initiator alone. (b) Run 5: dilithium initiator with 9.4% s-BuLi.

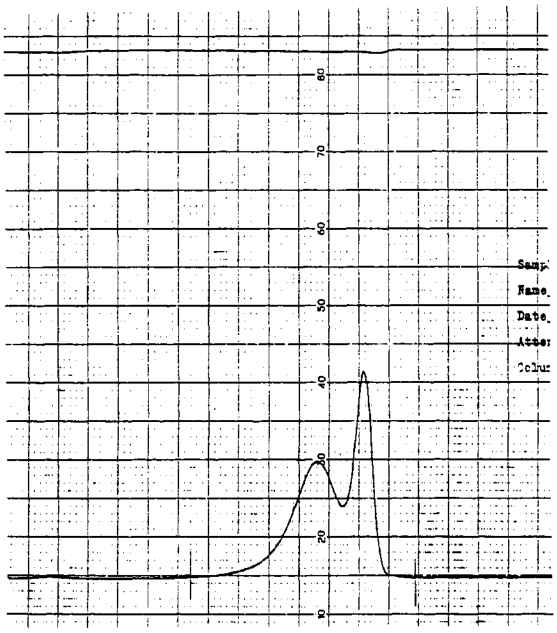


Figure 6. GPC chromatogram of the polyisoprene from run 5 initiated by a dilithium initiator mixed with 9.4 mol % s-BuLi.

in Figure 5b. The first small exotherm can be attributed to the heat of isoprene polymerization initiated by the monofunctional initiating s-BuLi. The major exothermic peak started a little quicker than that in the first isoprene run. There was again a match in time between the appearance of the broad major peak in the GPC chromatograms and the second rise in the temperature profile. In the chromatogram of the final polymer, shown in Figure 6, the two peaks of the bimodal distribution are much closer in molecular weight than those in the final polymer of run 1. The size of the high molecular weight peak was larger which is consistent with the conclusion that the high molecular weight peak was derived from monofunctional initiation.

In isoprene polymerization run 6, the dilithium initiator was made with an excess of PEB. In cyclohexane, s-BuLi adds faster to the second double bond on PEB than the first.[1,2] As a result the initiator solution, as measured by GC, contained 5.4% PEB, 2.5% monoadduct of s-BuLi with PEB, and 92.1% diadduct—more unreacted PEB than monoadduct. The GPC chromatogram of the final polymer is shown in Figure 7. As expected the high molecular weight peak was not nearly as large as in the run made with 9.4% excess of s-BuLi in the initiator because there was only 2.5% monoadduct that might function as monofunctional initiator. The chromatogram had a high molecular weight shoulder not seen before. The double bonds on the excess PEB and the monoadduct both could react to create a high molecular weight material, the former as a cross-linker and the latter as a chain-branching agent. However, the double bond in the form of a 1,1-diphenylethylene functionality must have reacted very slowly with polyisoprenyl anions. Otherwise, the 5.4 mol % PEB would have gelled the polyisoprene.

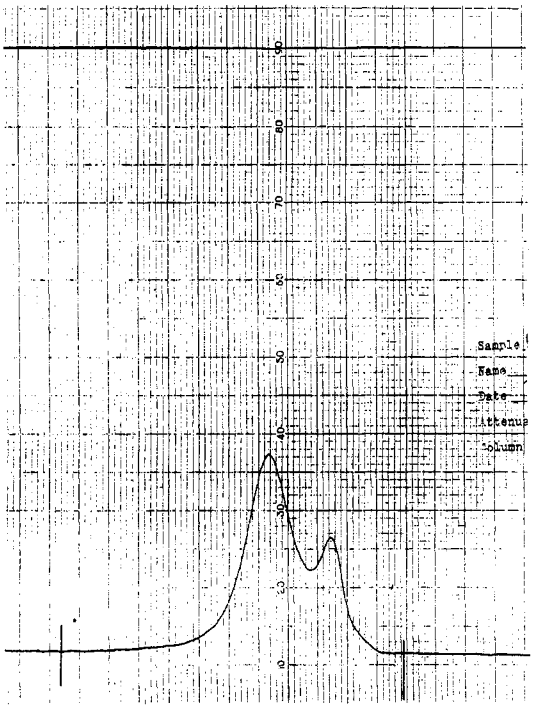


Figure 7. GPC chromatogram of the polyisoprene from run 6 initiated by a dilithium initiator prepared with an excess of PEB.

The last isoprene polymerization run, run 7, was made with a dilithium initiator partially terminated with about 25 mol % methanol. The same peak development as in other isoprene runs was observed. Interestingly, the high molecular weight peak of the final polyisoprene of this run as shown in Figure 8 was not as large as that in run 5. If the two initiating sites on the dilithium initiator were protonated by methanol at equal rates and if instant mixing was achieved in the methanol addition, the 25 mol % methanol would have generated 37.5% singly protonated, 6.3% doubly protonated, and 56.2% unreacted initiator. The monofunctional initiating species generated in this run was less than the 9.4% excess of s-BuLi in run 5 and obviously much lower than the theoretical 37.5%. Mixing, however imperfect, is unlikely to have accounted for this large discrepancy. The second site on the initiator therefore could be more reactive toward methanol than the first. This latter effect was indicated also by the results in an aging study of the dilithium initiators reported earlier.[1]

The result in polymerization run 4 showed that even when nearly all impurities in the feed were blanked out there was still more monofunctional initiating species than that could be accounted for by the amount of monoadduct in the initiator. Run 7 showed that the impurities in the feed might not have generated a large amount of mono-

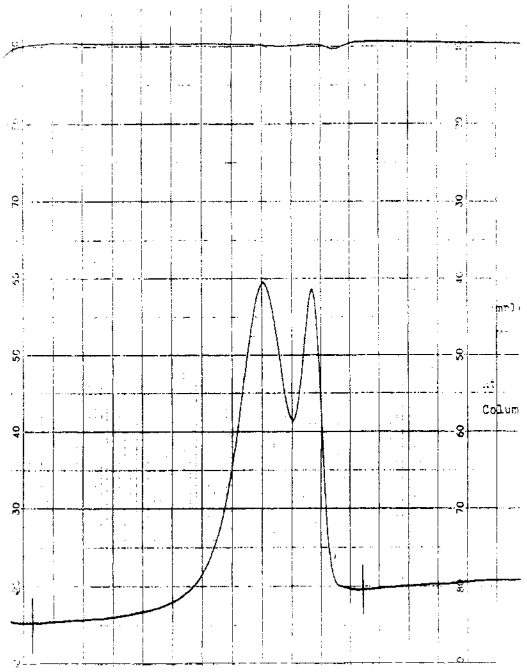


Figure 8. GPC chromatogram of the polyisoprene from run 7 initiated by a dilithium initiator partially terminated by methanol.

functional initiating species since instant mixing would not be possible and the second site on the initiator might be protonated earlier than the first. There is therefore a doubt whether a third source other than the two already mentioned could have contributed to the amount of monofunctional initiating species observed in a normal run such as run 1. A reverse reaction was observed[8] in the addition reaction of oligomeric poly(styryllithium) with a double 1,1-diphenylethylene compound, bis[4-(1-phenylethenyl)phenyl] ether. If the same reverse reaction happened also in the addition reaction of s-BuLi with PEB or MPEB, s-BuLi and monoadduct would have been generated and both would have contributed to the total monofunctional initiation.

To test whether there was such a reversibility, 4.0 mmol of 1,1-diphenylethylene was added to a solution containing 1.7 mmol of a dilithium initiator based on PEB. The mixture was allowed to stir for 4 h at 50 °C and then stand overnight at room temperature. If any s-BuLi was freed in the system, it would add to the 1,1-diphenylethylene, whereas the dilithium initiator itself would not add. No evidence for any addition product of s-BuLi to 1,1-diphenylethylene was found by GC analysis. As a control run, 0.09 mmol of s-BuLi was added to a solution containing 1.2 mmol of dilithium initiator and 3.0 mmol of 1,1-diphenylethylene. After 2 h at 50 °C a significant amount of addition product of s-BuLi to 1,1-diphenylethylene was found by GC.

Discussion. The polymerization experiments in this work were not carried out under isothermal conditions, and high-vacuum techniques were not used to assure minimal contamination. Quantitative treatment of the data with high precision and accuracy was not a goal. However, the results were sufficient to establish that the high molecular weight peak of the bimodal distribution was mainly polyisoprene from monofunctional initiation, that the dilithium initiator quickly reacted with isoprene to form an adduct, and that further polymerization from the adduct was very slow.

The main source of monofunctional initiating species appeared to be the partially terminated dilithium initiator. By blanking the feed, monofunctional initiation as low as 2.6 mol % was achieved in run 5. Still lower amounts of monofunctional initiation should be attainable by additional steps to control the experimental conditions more carefully. The monoadduct of s-BuLi and PEB, another source of monofunctional initiation, could also possibly be reduced by more careful initiator preparation and handling. The dilithium initiator did not revert back to s-BuLi and monoadduct to become a source of monofunctional initiation.

The temperature profiles of the runs indicated that the molecular weight difference between the two peaks of the bimodal distribution could be reduced by the manipulation of polymerization temperatures. If the high molecular weight peak was made closer to that of the main peak, the same mole percent of monofunctional initiation would have produced a lesser amount by weight of monofunctional materials. In a triblock, the diblock contamination would be smaller and the strength would be higher. In isoprene polymerization run 1, the 6 mol % monofunctional initiation produced 27 wt % material in the final polymer. If the two peaks were at the same molecular weight in SIS polymerization, then the weight of the diblock would have been only 6%, which should not cause a great loss of tensile strength. It is plausible that, in the polymerization of butadiene, the broad distribution observed[1] was a bimodal distribution with the two peaks, one from difunctional initiation and one from monofunctional initiation, very closely spaced. The good strength in SBS could be explained by the fact that the weight percent of diblock, because of the closeness of the two peaks, was not high enough to severely damage the tensile properties. The sensitivity of the molecular weight distribution to experimental conditions in the butadiene polymerization observed earlier could be explained by the fact that the molecular weight difference between the two peaks was sensitive to the temperature profile. The polymerization solution temperature for the most part was higher than the controlled jacket temperature and not always exactly reproducible.

The above view is not at variance with the observation by Quirk and Ma,[4] who reported bimodal distribution in low molecular weight polybutadiene and monomodal distribution in higher molecular weight polybutadiene. Neither is the view at variance with Broske et al.,[2] who observed narrow distribution at low molecular weight but broader distribution at higher molecular weight. Quirk and Broske both used high-vacuum techniques. Contamination by impurities in their systems should be at a minimum. In the case of Quirk and Ma, they monitored their initiator composition chromatographically until all PEB was consumed. However, they probably could not detect small excesses of s-BuLi which would have become a source of monofunctional initiation. For low molecular weight polybutadiene, the monofunctional initiated material was a significant portion of the entire sample and hence the bimodal distribution. At high molecular weight the main peak would have overlapped the high molecular weight peak and the distribution became monomodal. In the case of Broske et al., a slight excess of PEB would not have produced significant monofunctional initiation in view of the fast reaction of the second double bond of PEB with s-BuLi. The slight excess of PEB in butadiene polymerization, however, would have caused cross-linking at high molecular weight and a broadening of the distribution.

Yamagishi et al.[9] suggested a dimeric association of the dilithium initiator prepared by the reaction of poly(styrylithium) with the double 1,1-diphenylethylene compound, 4,4′-bis(1-phenylethenyl)-1,1′-biphenyl. The dimeric ring was inert and was in equilibrium with an open form which initiated polymerization. The quick formation of the initiator–isoprene adduct suggests that the dimeric ring form of the dilithium initiators based on the addition of s-BuLi to PEB and MPEB, if it existed, shifted readily to the reactive open form. The resulting isoprenyllithium, with a large dilithium initiator molecule attached, formed another inert association which was much more favored than the reactive form in equilibrium with it.

The inertness of the oligomeric initiator–isoprene adduct is in agreement with the kinetic study by Madani et al.[7] on another dilithium initiator. Madani et al. observed autoacceleration in isoprene polymerization from difunctional oligomeric isoprenyllithium. The extent of autoacceleration decreased with the increase of the initiator concentration. The initiator concentrations used in our work were at about 1×10^{-3} M where distinct autoacceleration was observed by Madani. Madani used a DP 20 isoprenyldilithium for their kinetic work. Our adduct with only 2–3 isoprenes attached should start at an even slower propagation rate. The concentration dependence observed by Madani suggested that intramolecular association should be responsible for the autoaccleration phenomenon. The "melting" of peak A into the formation of peak C, shown in Figure 1, may very well be a manifestation of the autoacceleration phenomenon. It appears that the slowness of the oligomeric initiator–isoprene adduct to propagate may be a general phenomenon for all dilithium polymerizations.

The data in this work suggested that high strength SIS may be obtained by the manipulation of the polymerization conditions. The successful application of seeding[5] and the uses of polar additives[1,5] are the examples.

The data suggested also that, in dilithium initiator preparation, error on the side of excess PEB (or MPEB) in stoichiometric matching should be preferred. The small excesses in double bonds are not very reactive toward isoprenyl anions. However, in butadiene polymerization such an excess might cause undesirable cross-linking as reported by Quirk et al.[10]

Table 2 summarizes the polydispersity index M_w/M_n of the final polyisoprene of the five isoprene polymerizations. This index varied widely depending on the conditions in the polymerization and did not reflect the behavior of the dilithium initiator. Ranking of the efficiency of different initiators by this index, as was done by Bandermann et al.,[11] may lead to erroneous conclusions.

Table 2. M_w/M_n Ratios of Polyisoprene

run no.	condition	M_w/M_n
1	dilithium initiator used directly	2.06
4	feed blanked before initiation	1.83
5	excess s-BuLi in the initiator	1.58
6	excess PEB in the initiator	1.97
7	initiator partially terminated by MeOH	1.63

Experimental Section

Materials. Isoprene, supplied by Goodyear Tire and Rubber Co., was purified by passing through an activated alumina column and vacuum distilled in the presence of dibutylmagnesium before use. Styrene, commercial grade, was purified by passing through an activated alumina column and vacuum distilled in the presence of calcium hydride before use. Cyclohexane, distilled in glass grade, was purified by passing through activated alumina. Methanol and 2-propanol HPLC grades were supplied by the Fisher Scientific Co. s-BuLi, 12 wt % in cyclohexane, was obtained from the Lithium Corporation of America. The precise concentration of the s-BuLi solution was determined by the double titration method of Gilman.[6] 1,1-Diphenylethylene was purchased from Aldrich Chemical. Purification was carried out on a vacuum line by blanking the impurities with s-BuLi followed by distillation.

PEB was prepared in the laboratory by the isophthaloyl dichloride acylation of benzene in the presence of an equivalent amount of $AlCl_3$ to give the diketone which was then converted to PEB via methyl Grignard and dehydration reactions. The same procedure was used to prepare MPEB except that toluene instead of benzene was acylated. Crude PEB and MPEB were purified through recrystallization from methanol.

Preparation of Dilithium Initiators. Solutions of dilithium initiators were prepared by reacting 2 mol of s-BuLi with 1 mol of PEB or MPEB in cyclohexane. As a typical example, cyclohexane (355 mL) was added into a 500-mL stainless steel tube and deaired by alternatively evacuating and admitting nitrogen six times. PEB (8.04 g, 28.47 mmol) was weighed into a 250-mL flask, and cyclohexane (30 mL) was added. The solution was deaired and transferred into the stainless steel tube by syringe. Cyclohexane (40 mL) was again added to wash the flask, deaired, and transferred into the tube. A s-BuLi solution in cyclohexane (37.8 mL, 56.10 mmol) was then added to the stainless steel tube. The tube was shaken to mix the solution, heated to 45–50 °C for 1 h, and then placed on top of a warm oven overnight to maintain the solution temperature at 35–40 °C. The resulting initiator was analyzed by GC, and its concentration which was approximately 0.06 mol/L was determined by the double titration method of Gilman.[6]

Before each use, the initiator solution was transferred into a flask which was under a nitrogen atmosphere. The exact amount of the initiator solution was then transferred from the flask to the reactor by a syringe.

Polymerizations. A 1.3-L jacketed reactor described earlier[1] was used for all the polymerizations. Cyclohexane was added to the reactor from a holding tank through an activated alumina column. The solution was deaired by alternately evacuating and admitting nitrogen three times. Isoprene was added through another inlet of the reactor by a syringe against a slight nitrogen pressure. The jacket temperature was set at 55 °C to start the heating of the reaction solution. When the solution temperature reached about 53 °C, the required initiator solution was added. A nitrogen pressure of 10–14 psi was maintained in the head space of the reactor during the polymerization. The exothermic heat from isoprene polymerization would drive the temperature of the solution to a maximum 15–20 °C above the jacket temperature in about 25–30 min after initiation. After the temperature began to subside, the jacket temperature was raised to 65 °C. Polymerization was allowd to continue for another 30–40 min before 0.2 mL of 2-propanol was added to terminate the polymerization. Samples periodically taken during the polymerization were terminated individually with 2-propanol before exposure to air. Percent monomer conversion was calculated from the percent solids determination on the samples.

Polymer Fractionation Procedures. Isolation of the initiator–isoprene adducts from polymerization run 2 was carried out by first removing the solvents from the polymer sample solutions (approximately 200 mL in size) under a nitrogen purge and mild heating conditions. Approximately 0.5 g of the solids was used for the fractionations. The first step was to remove as much of the lithium salts as possible by extracting the solid with 5 mL of cyclohexane and 1 mL of acetone. The gelatinous solid was separated from the solution and extracted twice with 2 mL of fresh cyclohexane. All of the soluble fractions were combined and centrifuged to remove any residual lithium salts. To the supernatant solution was added slowly with stirring 25 mL of acetone to precipitate the higher molecular weight polymer fraction (at about 10 mL of acetone addition, the solution became cloudy). The solution was then centrifuged to separate the soluble fraction from the precipitated fraction. Both fractions were dried in order to obtain actual weights. The soluble fraction was used for GPC and NMR analyses.

Isolation of the high molecular weight styrene–isoprene block copolymer in polymerization run 3 was done by a different procedure. Approximately 1 L of a 2-propanol-terminated polymer solution was used for the fractionation. About 500 mL of acetone was slowly added to the polymer solution with agitation. 2-Propanol, approximately 500 mL, was then slowly added with intensive agitation until the polymer solution became cloudy.

After letting the solution settle into two layers overnight, the solution was decanted from the precipitate on the bottom. The precipitate was redissolved in 100 mL of methylene chloride. Acetone was added to the redissolved polymer solution with good agitation until the polymer was again precipitated. This step was repeated once more, and the polymer recovered was vacuum dried for GPC analysis and mechanical property testing.

Analysis. A Hewlett-Packard Model 5840A instrument with a 12-m OV-101 methyl silicone capillary column was used for GC determinations.

The ^{1}H NMR spectra were determined on a Varian EM-390 spectrometer operating at 90 MHz. Polymer samples were prepared as ca. 12% w/v in chloroform-*d*.

Gel permeation chromatography (GPC) measurements were made on a Waters 150C GPC instrument equipped with six Varian MicroPak TSK columns (three single pore and three mixed bed) and a UV photometer as the second detector.

Tensile properties of the triblock copolymer were tested at 23 °C on compression-molded specimens. The 0.025-in.-thick 3-in.-long dumbbell-shaped specimens were cut from the molded sheet. The cross-head speed was 20 in./min.

Conclusions

The bimodal molecular weight distribution in polyisoprene was mainly the result of the inadvertent presence of monofunctional initiating species in the reaction mixture. Polymerization of isoprene from the monofunctional initiating species was faster than the polymerization from the dilithium initiator and formed the sharp high molecular weight peak in the bimodal distribution of the final polymer.

The initiation of isoprene by the dilithium initiator may not be very slow. Chain propagation from the initial oligomeric isoprene attached to the dilithium initiator was much slower. Growth from this initial initiator–isoprene adduct was the rate-controlling step that caused the formation of the second peak of the bimodal distribution.

The organodilithium initiator itself may exist as an inert dimeric ring form in equilibrium with a reactive open ring form. Fast attachment of isoprene units to the initiator indicated that the shift from the inert dimeric form, if it existed, to the reactive form was relatively swift. The association of oligomeric isoprenyllithium derived from the dilithium initiator must be tighter and its shift to the reactive form more difficult. Likely the association is intramolecular as suggested by Madani et al. This behavior is likely to be common to all dilithium-initiated polymerizations.

A major source of the monofunctional initiating species was identified to be the dilithium initiator terminated partially by the impurities in the polymerization system. Therefore, it should be possible to reduce the monofunctional initiating to a negligible amount by careful experimentation and thereby to produce a nearly monomodal distribution polyisoprene.

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