Determination of Solution Polymerization Kinetics by Near-Infrared Spectroscopy. 1. Living Anionic Polymerization Processes

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ABSTRACT: Near-infrared (NIR) spectroscopy (1.0–2.5 μm or 10 000–4000 cm^{-1}) was successfully utilized to monitor monomer conversion during conventional, anionic solution polymerization. The conversion of the vinyl protons in the monomer to methylene protons in the polymer was easily monitored under conventional (10–20% solids) solution polymerization conditions. Despite the presence of the NIR probe, the "living" nature of the polymerizations was maintained in all cases. Both styrene and isoprene polymerization kinetics were investigated in nonpolar and polar solvents, and relative rate constants were compared to values previously reported in the literature. In addition to the need for an inert probe, high sampling frequencies were required since polymerization times ranged from 5 s in tetrahydrofuran to 20 min in cyclohexane. Copolymerization kinetics have also been studied in order to determine the feasibility of NIR as an on-line structural probe. In fact, preliminary data indicate that NIR is capable of detecting sequence distributions for tapered block copolymers, geometric isomer content, and reactivity ratios for free-radical copolymerization. Future studies will focus on the application of NIR to elucidate polymerization mechanisms and deleterious side reactions.

Introduction

Living polymerization processes permit the synthesis of well-defined macromolecules with controlled chemical composition, predictable molecular weight, and narrow molecular weight distribution.[1,2] Demonstration of the living nature of a polymerization is usually accomplished by a linear plot of number-average molecular weight versus conversion. Due to the absence of side reactions that terminate propagation, complete conversion of monomer is always obtained. The data are generally obtained by careful sampling techniques followed by gravimetric and size-exclusion chromatographic analyses. Alternatively, samples can be withdrawn from the reactor and analyzed for residual monomer in solution at various times by chromatographic or spectroscopic techniques.[3] Sample sizes and the frequency of sample withdrawal are generally limited by the polymerization scale.

There are mainly four techniques that thave been used in the past to obtain kinetic data on anionic polymerization processes: sampling, dilatometry, stop-flow, and capillary flow.[4,5] Techniques such as dilatometry, stop-flow, and capillary flow are very tedious and require specially designed reactor systems. Sample removal techniques are very difficult since anionic polymerizations are sensitive to atmospheric water and oxygen. It is very easy to introduce small quantities of impurities during sampling, which broaden molecular weight distributions and result in a nonrepresentative sample. Sampling techniques are also impossible to perform for the analysis of fast monomer conversion rates (less than 1 min). Anionic polymerizations in polar solvents are typically complete within seconds after initiation. Consequently, it would be very desirable for the synthetic polymer chemist to have real-time access of monomer conversion and kinetic information without sampling.

Near-infrared (NIR) spectroscopy is well suited to provide real-time structural and kinetic data without complicated hardware or techniques.[6,7] A fiber optic probe can be simply inserted into an existing reactor system without time-consuming, expensive, and unrealistic hardware modifications. Fiber optics technology allows the spectrophotometer and computer to be located away from the reactor process. Remote monitoring is very desirable when it is not acceptable to have electrical equipment located adjacent to the reactor. Most NIR absorbances are overtone or combination bands of fundamental bands and are typically weaker than their corresponding fundamental transitions.[8,9] Consequently, in general NIR may not be suitable for minor component analysis. On the other hand, lower extinction coefficients simplify sample preparation since it is easier to obtain a linear Beer's law relationship at higher concentrations. NIR also permits facile subtraction of the polymerization solvent background, and conventional solution concentrations are acceptable. Some disadvantages are that the monomers of interest must have absorbances in the near-infrared region, and it is most desirable if they do not overlap with each other. Individual NIR absorbance bands are also difficult to identify, and selectivity can be lost in some cases due to band overlap. Multivariate calibration procedures can be implemented to account for NIR band overlap; however, its success depends on the degree of overlap and the level of system understanding.

Other workers have reported the utility of NIR for the characterization of polymer structure. In most cases, samples were characterized in the bulk form, not as a real-time probe during solution polymerization. For instances, cross-linking reactions of epoxy resins[10] have been monitored by watching the disappearance of epoxide groups at 4532 cm^{-1}. In addition, a recent report demonstrates the use of NIR to monitor methyl methacrylate conversion in a bulk free-radical polymerization.[11] Also, NIR was utilized to monitor the kinetics of high-pressure ethylene polymerizations.[12] The ethylene and polyethylene concentrations were determined from absorption bands near 6000 and 8800 cm^{-1}, respectively. Conventional mid-infrared spectroscopy (4000–600 cm^{-1}) has been used to monitor the kinetics of *N*-carboxyanhydride polymerizations to amino acids.[13]

This work demonstrates the feasibility of NIR as a suitable real-time monitoring technique for solution

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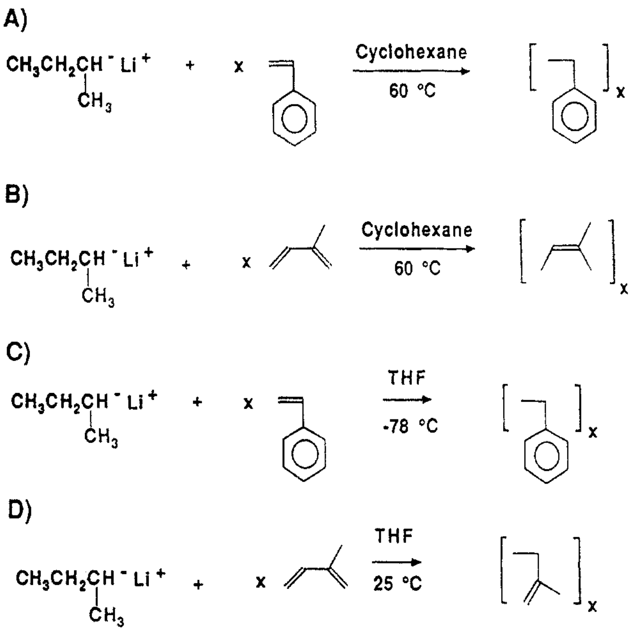
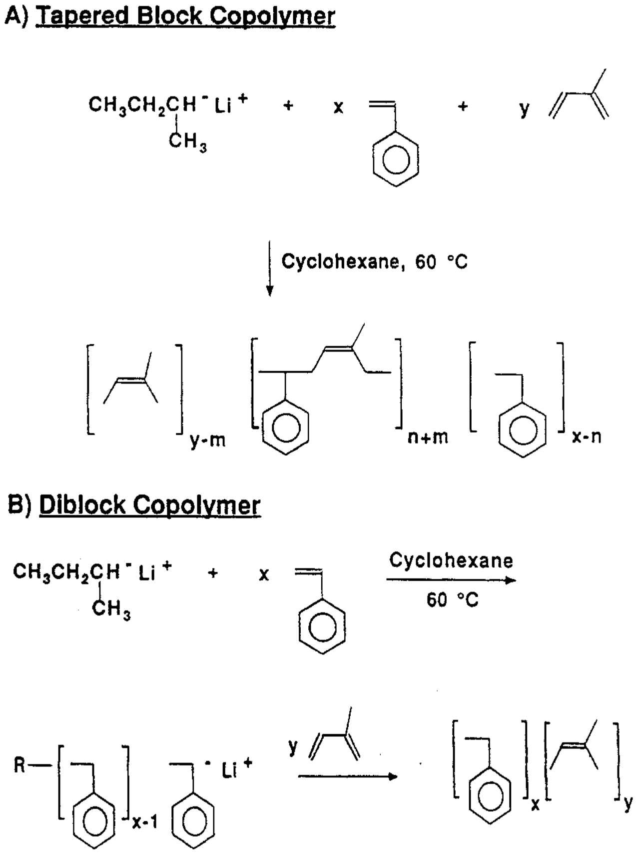
Scheme I. Synthesis of Polyisoprene and Polystyrene Homopolymers via Anionic Polymerization in Polar and Nonpolar Solvents



Scheme II. Copolymerization of Isoprene and Styrene via Anionic Polymerization in Cyclohexane at 60 °C



polymerization processes. In particular, this technique will be applied to living anionic polymerization processes. An attempt will be made to demonstrate the versatility of the techniques by monitoring an existing polymerization reactor system without any modifications to the process except for the presence of the NIR probe.

Experimental Section

Materials and Purification. Isoprene (Eastman Kodak Co.) was degassed with ultrapure nitrogen and passed through columns of activated basic alumina and molecular sieves immediately prior to use.

Styrene (Aldrich) was vacuum distilled from calcium hydride and stored under nitrogen in a freezer at -25 °C. An additional vacuum distillation from dibutylmagnesium was performed just before use.

Cyclohexane was stirred over concentrated sulfuric acid for several days, decanted, and distilled under nitrogen from a sodium dispersion in paraffin.

Tetrahydrofuran was distilled under ultrapure nitrogen from the classical sodium benzophenone ketyl drying reagent. The solvent was stored in a septum-covered, round-bottomed flask under positive nitrogen pressure.

Polymerizations. Schemes I and II depict the synthetic strategies for various homo- and copolymer processes, respectively, that were monitored by NIR. The experimental details are described in detail below.

Cyclohexane Solvent. Polymerizations in cyclohexane were carried out at 60 °C in a small-scale reactor system described previously.[14] The NIR probe was connected to the reactor using Swagelock fittings through a spare, $^{1}/_{4}$-in., threaded hole on the top plate of the reactor.

Polystyrene Homopolymers. The reactor was charged with styrene that had been distilled only from calcium hydride, and *sec*-butyllithium (FMC) was employed as both a purification reagent and anionic initiator. Taking advantage of the relatively slow polymerization rate in this solvent, impurities were slowly titrated until the first faint color of the poly(styryllithium) anion persisted, and the desired amount of initiator was quickly added. Polymerization progress was followed by scanning over the spectral window from 1.1 to 1.7 μm at 1-min intervals and observing the decrease in the monomer vinyl C–H overtone band. The spectrum also contained a vinyl combination band superimposed on an aromatic absorption. The polymerization was terminated with degassed, HPLC-grade methanol. The polymer was precipitated into a 50:50 (v/v) mixture of methanol and isopropyl alcohol, filtered, and dried in vacuo overnight at 80 °C.

Polyisoprene Homopolymers. Polymerizations were conducted and monitored in the same manner as the styrene homopolymers. Polymers were worked up by removing most of the solvent by rotary evaporation, adding 0.1 wt % antioxidant (Irganox 1010, Ciba-Geigy Corp.), and then removing residual solvent in vacuo at room temperature.

Poly(styrene-*b*-isoprene) Block Copolymers. Copolymers were synthesized by sequential addition of isoprene to a living solution of poly(styryllithium) in cyclohexane at 60 °C when the first monomer was determined to have been depleted. Isolation and purification were identical to the styrene homopolymers.

Poly(styrene-*tb*-isoprene) Tapered Block Copolymers. Equal weights of the freshly purified monomers were mixed in the reactor and initiated. As the polymerization was monitored by NIR, it was visually observed to change gradually from the initial pale yellow of the poly(isoprenyllithium) anion to the orange of poly(styryllithium).

Tetrahydrofuran (THF) Solvent. Polymerizations in THF were run in a 500-mL, two-necked, round-bottomed flask fitted with rubber septa. The NIR probe was introduced through a small hole in one of the septa and a nitrogen purge needle inserted alongside the probe to maintain pressure. All reactions involving styrene were conducted at -78 °C (dry ice/isopropyl alcohol bath), while isoprene polymerizations were allowed to warm to room temperature (switching to a water bath) after initiation at -78 °C.

The same experiments as outlined above in cyclohexane were conducted in THF. Styrene-containing polymers were isolated by precipitation into methanol, while the workup of polyisoprenes was identical to that of polymers produced in cyclohexane.

Because of the extremely fast polymerization rate of styrene in polar solvents, it was not possible to obtain a full absorbance versus wavelength spectrum with the existing instrumentation. In this case, the reaction progress was followed by observing the decrease in monomer absorption at a single wavelength. Readings were taken at 0.1-s intervals at the peak maximum located at 1.624 μm. A utility program was provided by Guided Wave Inc., which actually scans over a very narrow wavelength region (1-2

Table I. Representative Molecular Weights ($\bar{M}_n$) and Molecular Weight Distributions ($\bar{M}_w/\bar{M}_n$) of Various Polymers Produced during Real-Time NIR Monitoring

polymer sample	$\bar{M}_n$(theo)	$\bar{M}_n$(SEC)[a]	$\bar{M}_w/\bar{M}_n$[a]
polystyrene	10 000	9 200	1.09
poly(1,4-isoprene)	10 000	9 600	1.13
poly(styrene-*b*-3,4-isoprene)	20 000	26 100	1.25
poly(isoprene-*tb*-styrene)	20 000	23 000	1.05

[a] Determined by size-exclusion chromatography (SEC) in THF with viscometric and light scattering detectors.

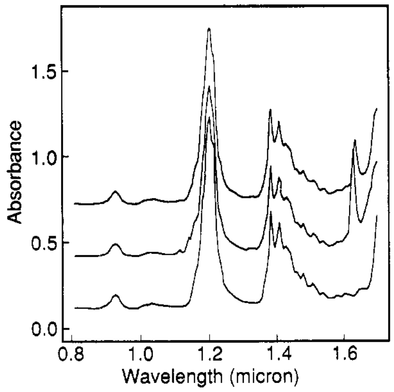


Figure 1. NIR spectra of cyclohexane (bottom), 10% isoprene monomer in cyclohexane (center), and 10% poly(3,4-isoprene) in cyclohexane (top) at 25 °C.

nm). Since the polymerization of isoprene remains relatively slow in THF, complete spectra of isoprene homopolymerizations, and the isoprene stage of copolymerizations, could still be obtained.

Polymer Molecular Weight and Molecular Weight Distribution Characterization. Table I summarizes molecular weights and molecular weight distributions of various homopolymers, block copolymers, and tapered block copolymers produced during NIR monitoring.

Near-Infrared Instrumentation. NIR spectra were measured using a Guided Wave Model 260 scanning spectrophotometer (Guide Wave, Inc.), which is equipped with a thermoelectrically cooled Ge detector and an optical probe (1-1W460-8B). This fiber probe has one excitation and one observation fiber with a rhodium reflective surface. The optical path (2 times the distance between the bider tip and the reflective surface) is about 1 cm. This spectrometer is capable of collecting the whole visible and near-infrared spectrum or monitoring the absorbance of a selected wavelength as a function of time. The length of the fiber optic from the spectrometer to the reactor was approximately 5 m, although we have observed that lengths greater than 100 m still provide acceptable signal to noise.

Results and Discussion

The successful use of an on-line spectroscopic polymerization monitor requires that the absorbance bands of the monomer, polymer, and polymerization solvent do not overlap. Consequently, initial experiments involved the analysis of the NIR spectrum of each component. Figure 1 depicts three NIR spectra: cyclohexane (bottom), 10% isoprene monomer in cyclohexane (center), and 10% poly(3,4-isoprene) in cyclohexane (top). Typical polymerization conditions for isoprene are 8–10% monomer concentrations in cyclohexane at 60 °C, and an attempt was made to model these conditions to determine feasibility. Another important criteron is the ability to subtract the solvent absorbances in order to facilitate monomer conversion analysis. Prior to the addition of monomer, the solvent spectrum was scanned and used as the reference instead of air. Figure 2 illustrates that cyclohexane was easily subtracted from the monomer spectrum (bottom) and the poly(3,4-isoprene) spectrum (top). Thus, real-time subtraction could be performed and permit the visualization of monomer depletion as a function of time. It is evident in both Figures 1 and 2 that isoprene monomer has a useful, characteristic absorbance at approximately 1.624 μm. This absorbance has been assigned to the two pairs of vinyl carbon–hydrogen bonds ($H_2C{=}C$) in the diene monomer. It should be noted that the vinyl band in the poly(3,4-isoprene) is located in the same position as the vinyl in the monomer.

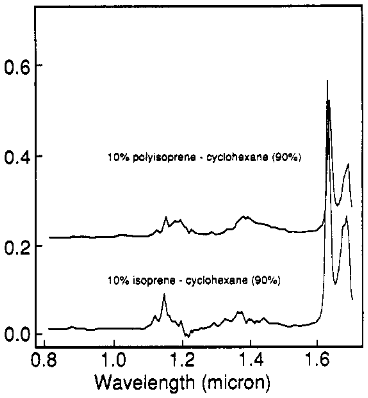


Figure 2. NIR spectra of isoprene monomer (bottom) and poly(3,4-isoprene) homopolymer (top) by subtraction of the cyclohexane spectrum at 25 °C.

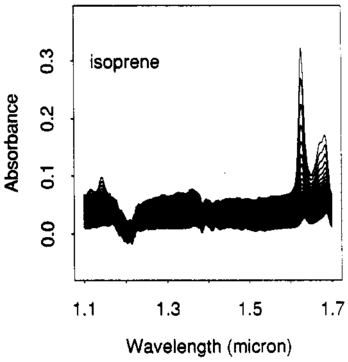


Figure 3. NIR spectra (1.1–1.7 μm) as a function of time for isoprene homopolymerization in cyclohexane at 60 °C.

In Figure 3 are spectra as a function of time for an isoprene homopolymerization in cyclohexane at 60 °C. A complete spectrum over this spectral range (1.1–1.7 μm) was taken every minute. Although the isoprene monomer absorption decreased substantially, a small percentage of the band remained after complete conversion. The residual vinyl absorption is attributed to the typical 8% 3,4-addition that occurs under these reaction conditions. The pendant vinyl group was easily detected by proton NMR. It is important to mention that the spectra in Figure 3 (formation of poly(1,4-isoprene)) differ significantly from the spectra in Figures 1 and 2, which are of poly(3,4-isoprene) (synthesized in THF). There are significantly higher levels of pendant vinyl groups in poly(3,4-isoprene). Proton NMR confirms that the poly(3,4-isoprene) (used in Figures 1 and 2) contains approximately 60% 3,4-addition, 30% 1,2-addition, and 10% 1,4-addition. Although our initial goal was to detect only monomer conversion with time, the real-time monitoring also of geometric isomer ratios is clearly both possible and potentially useful. Other workers have successfully used NIR coupled with a multivariate calibration approach to determine stereochemistry in polybutadiene samples.[15] In particular, information related to polymerization mechanisms may be obtained by monitoring the polymer stereochemistry as a function of time. Figure 4 simply

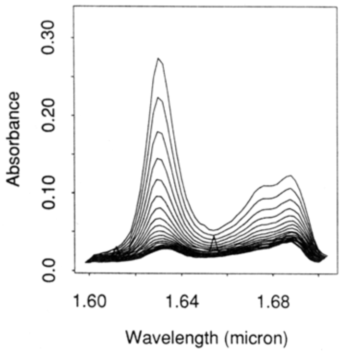


Figure 4. NIR spectra as a function of time for the synthesis of poly(1,4-isoprene) in cyclohexane at 60 °C.

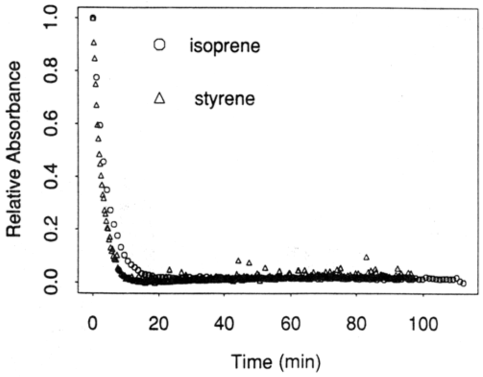


Figure 5. Relative absorbance as a function of time for styrene and isoprene homopolymerizations in cyclohexane at 60 °C.

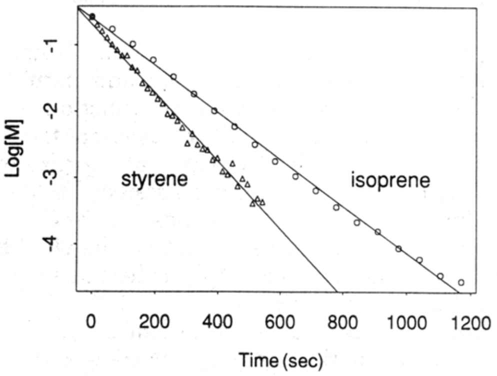


Figure 6. First-order kinetic plot of isoprene and styrene homopolymerization in cyclohexane at 60 °C.

depicts a narrower spectral window as a function of time for an isoprene polymerization. It is obvious that residual vinyl protons remain at the end of the polymerization.

Kinetic information is readily obtainable from the spectral data. The relative absorbance as a function of time can be plotted as exemplified in Figure 5. Figure 5 illustrates the decrease in absorbance versus time for both styrene and isoprene polymerizations (1.624 μm) in cyclohexane at 60 °C. Complete conversion was achieved within 20 min for both monomers. However, styrene conversion appeared to be slightly faster than isoprene. This would be predicted based on the lower activation energy required for the formation of a more delocalized carbanion. In order to confirm the validity of the technique and the data, a first-order kinetic plot was constructed for both isoprene and styrene. As expected, the plot in Figure 6 confirms that the anionic polymerizations of styrene and isoprene are first order relative to monomer. Since the anion concentration remained constant due to the living nature of the polymerization, the kinetic analyses were relatively simple. The calculated rate constants for propagation were 2 L mol^{-1} s^{-1} for styrene and 1.5 L mol^{-1} s^{-1} for isoprene. These values agree well with the literature, and the data are summarized in Table II.[16]

Table II. Experimental and Kinetic Data for Styrene and Isoprene Homopolymerizations in Cyclohexane at 60 °C

monomer	M (g/mL)	I (mol)	S (mL)	k_p (L mol^{-1} s^{-1})
styrene	28.6	0.002 88	440	2.0
isoprene	28.6	0.002 88	440	1.5
styrene[a]				2.0

[a] Literature value.[15]

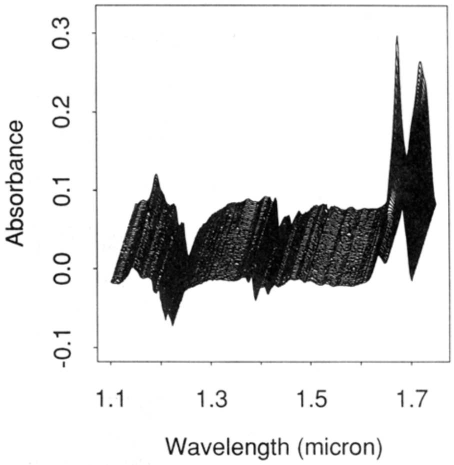


Figure 7. NIR spectra of mixed isoprene and styrene in cyclohexane at 60 °C as a function of polymerization time.

In addition to monitoring homopolymerization processes, it was postulated that copolymerization data could also be obtained in a real-time manner. Relative polymerization rates in copolymerization are conventionally described in terms of reactivity ratios wherein the ratio (r_1) is defined as the quotient of the rate constant for homopolymerization (k_{11}) to crossover (k_{12}).[17] Although reactivity ratios are generally associated with free-radical-initiated copolymerizations, reactivity ratios have also been determined for anionic polymerizations.[18] On-line NIR would provide both an indication of the "copolymerizability" of two monomers and the heterogeneity of the final polymer composition. This information would be valuable for determining the effect of polymer architecture on copolymer properties.

The copolymerization of isoprene and styrene was investigated in cyclohexane at 60 °C. It is known in the literature that these monomers when mixed and initiated with *sec*-butyllithium will form tapered block copolymers.[19] A tapered diblock copolymer unlike a true diblock copolymer contains an extended sequence of "random" copolymer between two long sequences of homopolymers. A representation of the tapered block copolymer structure is given in Scheme II. A complication arises when using NIR for the simultaneous analysis of these particular comonomers. The absorbances associated with the polymerizable double bonds (vinyl bonds) overlap. Solutions to this problem have been discovered and will be addressed in more detail. In Figure 7 are NIR spectra of mixed isoprene and styrene in cyclohexane at 60 °C as a function of polymerization time. Careful inspection of the monomer absorbance reveals that the rate of conversion is not constant. In order to probe this phenomenon more closely, a narrower spectral range was investigated. The data are presented in Figure 8. It is more evident that the rate of total monomer disappearance slows down during the reaction and then speeds up again. A plot of the total absorbance at 1.624 μm (peak maximum) versus time

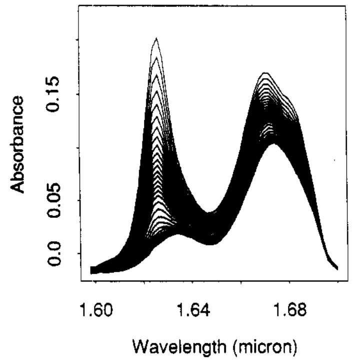


Figure 8. Narrow spectral range for mixed monomer polymerization in cyclohexane at 60 °C.

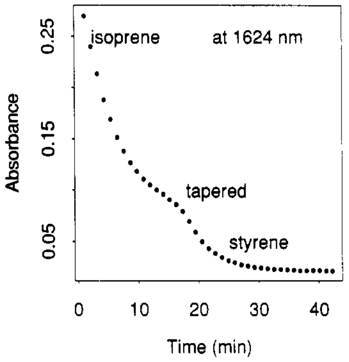


Figure 9. Total absorbance at 1.624 μm for mixed isoprene and styrene versus polymerization time.

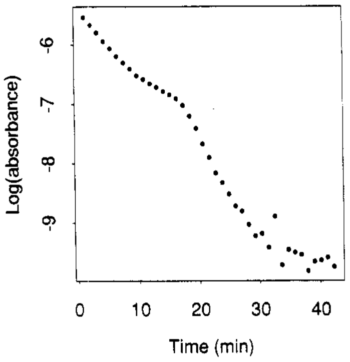


Figure 10. First-order kinetic plot for mixed styrene and isoprene polymerization in cyclohexane at 60 °C.

(Figure 9) clearly implies that two sequential rate constants are obtained. In a fashion similar to the homopolymerization studies, a first-order kinetic plot was constructed for the monomer pair (Figure 10). It is evident that the plot consists of more than one linear region and possibly an intermediate region. The isoprene polymerization most likely occurs first in the presence of styrene. This observation is consistent with the literature and with the appropriate color changes during the polymerization. The pale yellow poly(isoprenyllithium) anion persists for the first 10–20 min of the polymerization, and the color gradually turns to orange, which is characteristic of the highly delocalized poly(styryllithium) carbanion. The rate constants for each linear region are consistent with the rates for isoprene polymerization first, followed by styrene polymerization.

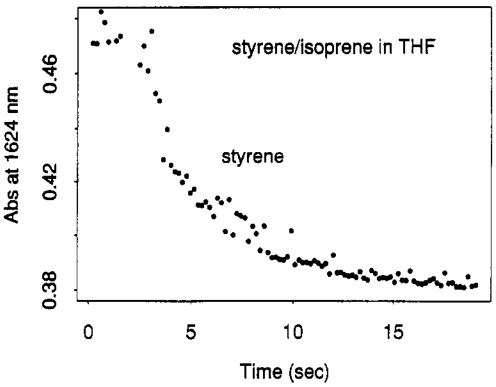


Figure 11. Disappearance of styrene monomer versus time in tetrahydrofuran at -78 °C.

The homo- and copolymerizations discussed above have focused on the use of a nonpolar polymerization solvent such as cyclohexane. In order to demonstrate the flexibility of NIR as an on-line probe, it was important to use other conventional polymerization solvents such as THF. Rate constants for anionic polymerizations in THF are more than 2 orders of magnitude greater due to solvation of the propagating anion.[20] Hence, in addition to probing the effect of polymerization solvent, "fast" polymerization rates were also a concern. In order to increase the rate of data acquisition, the absorbance maximum at 1.624 μm was monitored rather than the entire spectral range. Figure 11 depicts the disappearance of styrene monomer versus time in THF at -78 °C. It was observed that the polymerization is complete within 10–15 s after initiation. An adequate number of data points was collected despite the relatively fast polymerization kinetics. A linear first-order kinetic plot was obtained with a rate constant of 400 L mol^{-1} s^{-1}. This value is in good agreement with the literature value of 550 L mol^{-1} s^{-1} for a sodium naphthalene initiated polymerization of styrene (3×10^{-3} M) in THF at 25 °C. In a similar fashion, the homopolymerization of isoprene in THF was investigated under similar conditions, i.e., at -78 °C. However, it was determined that isoprene does not undergo polymerization in a convenient time at -78 °C. Consequently, the reactor was warmed to 25 °C for subsequent studies in order to promote the polymerization of isoprene in THF. The rate constant was determined to be 0.2 L mol^{-1} s^{-1} under these conditions. Although relatively narrow molecular weight distributions (M_w/M_n) were maintained (<1.25), reaction of the propagating carbanion with THF at 25 °C became a concern. The temperature change from -78 °C to room temperature did not effect our conclusions.

Copolymerization of isoprene and styrene in pure THF was investigated by monitoring the mixed monomer absorbance maximum. It is known in the literature that when THF is present at high levels (>1 wt %) styrene–isoprene random copolymers are obtained at 40 °C.[19] However, our experiment differed from literature in that the polymerization temperature was -78 °C. The absorbance at 1.624 μm versus time for the mixed monomers is plotted in Figure 12. It is clear that styrene undergoes polymerization first at -78 °C in THF and crosses over to isoprene. However, the polymerization of isoprene does not occur until after the polymerization temperature has been raised to room temperature. These observations were confirmed by noting the initial formation of the orange poly(styryllithium) carbanion, followed by a gradual change to the yellow–orange poly(isoprenyllithium) carbanion in THF. Due to the slower rate of isoprene polymerization compared to styrene in THF, the complete spectrum was monitored. Once again, we confirmed that the 1.624-μm NIR band is not affected by the change in solvent (cyclohexane versus THF) or temperature (-78 to 25 °C). This assumption may not be true for other solvents or different temperature ranges. Figure 13 shows the disappearance of isoprene at 25 °C in THF as a function of time. Once again, the final spectrum reveals the presence of residual vinyl carbon–hydrogen bonds, and,

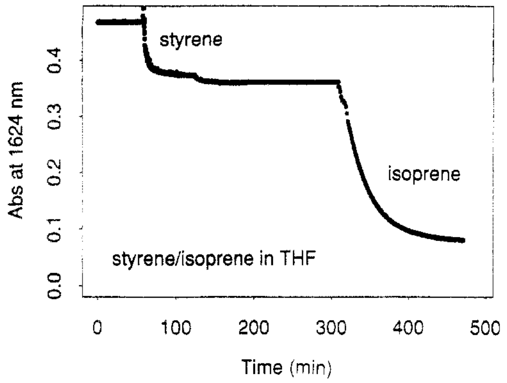


Figure 12. NIR absorbance versus time for mixed styrene and isoprene copolymerization in THF. Styrene polymerization was conducted at −78 °C, the reactor was gradually warmed to 25 °C, and the isoprene polymerization was monitored.

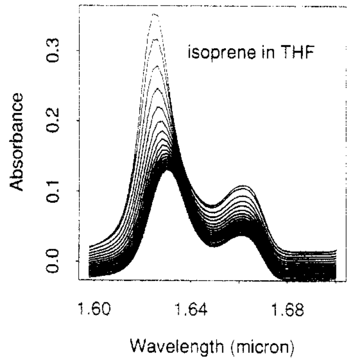


Figure 13. Disappearance of isoprene monomer as a function of time in tetrahydrofuran at 25 °C.

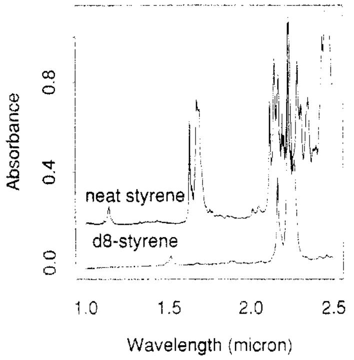


Figure 14. NIR spectra of perdeuterated styrene monomer (bottom) and styrene monomer (top).

at first glance, one would think the polymerization terminated. However, as discussed earlier, the residual absorbance was attributed to pendant vinyl substitution (3,4- and 1,2-addition) in the polymer.

Although the styrene–isoprene copolymerization studies were able to indicate the occurrence of tapering in cyclohexane and block copolymer formation in THF, it is more desirable to monitor nonoverlapping monomer absorbances. Styrene and isoprene represent the worst case scenario, as other comonomer pairs do not have overlapping absorbances (e.g., styrene and methyl methacrylate). Preliminary experiments have successfully monitored the free-radical copolymerization of 4-(*tert*-butoxycarbonyloxy)styrene (tBOC-styrene) and methyl methacrylate. Free-radical polymerization studies will be described in a future publication. Another solution to the overlapping absorbances is the use of deuterated monomers. Figure 14 illustrates the utility of deuterated styrene monomer. The absorbance of the vinyl carbon–deuterium bonds is significantly shifted away from the isoprene monomer absorbance. Consequently, the copolymerization of styrene and isoprene can be more closely monitored. The application of deuterated monomers in NIR analysis will be described in more detail later.

Conclusions

Near-infrared (NIR) spectroscopy (1.0–2.5 μm or 10 000–4000 cm^{-1}) was successfully utilized to monitor monomer conversion during conventional, anionic solution polymerization. The conversion of the vinyl protons in the monomer to methylene protons in the polymer was easily monitored under conventional (10–20% solids) solution polymerization conditions. Despite the presence of the NIR probe, the "living" nature of the polymerizations was maintained in all cases. Both styrene and isoprene polymerization kinetics were investigated in nonpolar and polar solvents, and relative rate constants were compared to values previously reported in the literature. In addition to the requirement for an inert probe, high sampling frequencies were required since polymerization times ranged from 5 s in tetrahydrofuran to 20 min in cyclohexane. Copolymerization kinetics have also been studied in order to determine the feasibility of NIR as an on-line structural probe. In fact, preliminary data indicate that NIR is capable of detecting sequence distributions for tapered block copolymers and reactivity ratios for free-radical copolymerization. Future studies will focus on the application of NIR to elucidate polymerization mechanisms and deleterious side reactions.

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