Microstructure of Alkyl Isocyanate Copolymers Comprised of Enantiomeric Monomers Determined by Desorption Chemical Ionization Mass Spectrometry

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ABSTRACT: The microstructure of copolymers generated from enantiomeric 2,6-dimethylheptyl isocyanate monomers was determined by desorption chemical ionization mass spectrometry (DCI-MS). (*R*)-2,6-Dimethylheptyl isocyanate and (*S*)-2,6-dimethyl-5,6-dideuteroheptyl isocyanate were prepared with the deuterium label incorporated into the (*S*)-monomer so that the (*R*)- and (*S*)-enantiomers could be distinguished by mass spectrometry. Homo- and copolymers of these enantiomers were prepared and examined by desorption chemical ionization, a method which causes depolymerization and generates protonated 1,3,5-tris(2,6-dimethylheptyl)cyanuric acids. The degree of deuterium incorporation into the (*S*)-monomer was determined by a tandem mass spectrometry procedure which avoids the errors associated with signals due to adventitious ions present in the single-stage mass spectra. The experiment involved mass selection and collision-induced dissociation of the entire isotopic envelope representing the (*S*)-trimer. This information was used to simulate the trimer region of the mass spectra of two copolymers, one containing 27% (*R*)-enantiomer and the other containing 74% (*R*)-enantiomer. Random and block structures were considered, and comparison with experiment revealed that the monomers are randomly distributed in the original copolymers. This analysis sets the stage for understanding the unusual nonlinearity between enantiomeric excess and optical activity in these copolymers and provides the first experimental correlation between the microstructure and the optical properties of synthetic D,L-copolymers.

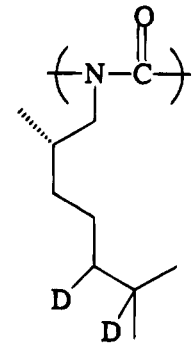
Introduction

Polyisocyanates are stiff high molecular weight polymers[1] which exhibit liquid crystalline properties.[2] Structural determination of various substituted polyisocyanates has been the subject of many studies.[3,4] On the local level, these polymers exhibit an extended rigid helix.[4] The ordered conformational characteristics of polyisocyanates is a trait which is similar to biological polymers where, in general, there are only a few allowed conformations.[5] This stands in contrast to most synthetic polymers which have a variety of local conformations that lead directly to their observed random-coil properties.[6,7]

Polymerization of alkyl isocyanates, in the absence of a chiral nonracemic side chain group, leads to the formation of both left- and right-handed helices with equal probability.[8] However, incorporation of a chiral alkyl substituent into the monomer induces a preferred helical sense in the polymer.[9,10] This phenomenon is well-known and shows itself in various ways.[11,12] A particular case, the homopolymer of poly((*R*)-2,6-dimethylheptyl isocyanate), adopts a left-handed helical conformation, while the homopolymer of the (*S*)-enantiomer takes a right-handed conformation.[2,12]

In this study, mass spectrometry is utilized in a novel manner to determine the microstructure of two copolymers comprised of different proportions of the (*R*)- and (*S*)-enantiomers of 2,6-dimethylheptyl isocyanate. This work is stimulated by the unusual nonlinear relationship between optical activity and enantiomeric excess in these copolymers, a phenomenon which requires knowledge of microstructure for its full understanding.[13,14]

Distinction between the enantiomers is accomplished by incorporation of a mirror-image selective label, deuterium, into the (*S*)-enantiomer. Using this label, it is possible for mass spectrometry to be used to differentiate the pyrolysates derived from poly((*S*)-2,6-dimethyl-5,6-dideuteroheptyl isocyanate) (**1**) and non-deuterated poly((*R*)-2,6-dimethylheptyl isocyanate) (**2**) as well as mixtures of the two monomers in oligomers of known size.



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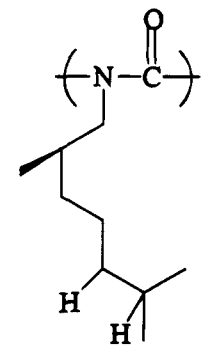

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Mass spectrometric analysis of polymers has been achieved using a variety of techniques[15] including pyrolysis gas chromatography/mass spectrometry (Py-GC/MS),[16-18] pyrolysis/mass spectrometry (Py-MS),[19,20] secondary ion mass spectrometry (SIMS),[21] fast atom bombardment (FAB),[22,23] and laser desorption (LD).[24] The softer methods of ionization such as SIMS, FAB, and LD, when performed under appropriate conditions, induce minimal fragmentation and therefore produce

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ions which are indicative of the molecular weight distribution. In contrast, deliberate degradation of the polymer is effected in Py-GC/MS and Py-MS methods in order to study the constituent monomers. Pyrolysis can be achieved by rapid inductive heating (10^2–10^4 K/s) (Curie-point pyrolysis),[25] laser irradiation,[26] and slow resistive heating.[27] In this study, a version of Py-MS, desorption chemical ionization mass spectrometry (DCI-MS), is used.[28] Resistive heating of the polymer on a rhenium wire filament induces pyrolysis while simultaneously desorbing the sample into the gas phase. The pyrolysates are then ionized, and the resulting protonated monomers or oligomers are mass analyzed.

Tandem mass spectrometry (MS/MS) has been widely used to provide structural information on target compounds in complex mixtures, including polymers.[29] This technique has recently been used to obtain structural information on polyethylene and polypropylene glycols,[30] polystyrenes,[31] polyamides,[32] *N*-alkylvinylpyridinium triflates,[33] and alkyl isocyanates.[34] DCI in combination with tandem mass spectrometry (DCI-MS/MS) and desorption electron impact tandem mass spectrometry (DEI-MS/MS) were used to characterize five major and three minor series of ions generated from *N*-alkylvinylpyridinium triflates. Ions in different series correspond to cleavage of different bonds between constituent monomers or hydrogen transfer in different directions.[31] Of particular interest here is the fact that alkyl isocyanates having *n*-hexyl, 2,6-dimethylheptyl, 3,7-dimethyloctyl, and (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl substituents can be characterized by DCI- and DEI-MS/MS. In this study, the tandem mass spectrometric analysis of polymers was extended to embrace the MS/MS/MS technique which employs three stages of mass analysis.[35] (This technique was implemented with a pentaquadrupole mass spectrometer.)[36] A major finding of the study is that DCI of alkyl isocyanates produce protonated 1,3,5-tris(alkyl)cyanuric acids, viz. the trimers, in high abundance and that these trimers fragment by α and β carbon–carbon bond cleavages and charge remote fragmentation. In addition, DCI-MS was used to determined the distribution of monomers in copolymers; for example, a copolymer comprised of *n*-hexyl isocyanate and 2,6-dimethylheptyl isocyanate in a 63/37 mole ratio was determined to have a random distribution of monomers. The possibility of randomization caused by substituent exchange in the gas phase was eliminated by recording DCI mass spectra of mixtures of various ratios of homopolymers and the finding that they produced no trimers with mixed substituents.[32]

Py-MS can be used to determine the monomer distribution in polymers, provided oligomeric units larger than the monomer are formed upon pyrolysis.[13,32] Using a Bernoullian statistical model, the distribution of monomer units in a polymer can be determined as being random or not. The monomer distributions of other types of polymeric systems are evaluated with first- or higher-order Markovian statistical models. Details of these statistical methods have been published elsewhere.[37–39] An example of a random distribution of monomers in a copolymer, as determined by DCI-MS, is described above in the case of alkyl isocyanates.[32] Evidence for a nonrandom distribution of monomers is provided by Markovian statistical analyses of the DCI mass spectra of polysiloxane copolymers.[40] In copolymers comprised of mirror-image monomers, the question of microstructure is of increased interest since conformational bias of each monomer toward one helical sense could act to perpetuate monomer selection of the growing chain to maintain the same helical sense. This would lead to a nonrandom incorporation of the mirror-image monomers into the polymer.

In the present study, many of these techniques are applied together with a unique application of DCI-MS/MS which is used to determine the actual deuterium incorporation into the (*S*)-2,6-dimethylheptyl-d_2 isocyanate. Isotopic incorporation into organic compounds is conventionally determined by recording the mass spectra of the labeled and unlabeled compounds under identical conditions which are also chosen to minimize fragmentation and ion/molecule reactions. This minimizes but does not eliminate ambiguities in the assignment of molecular compositions to ions resolved at unit mass and in the weighting of their contributions to the abundance at each mass value.[41,42] To determine the deuterium incorporation into the (*S*)-monomer as accurately as possible, the entire isotopic envelope of protonated (*S*)-1,3,5-tris(2,6-dimethyl-5,6-dideuteroheptyl)cyanuric acid was first mass selected and collisionally activated. The isotopic peaks of the (*S*)-monomer were then measured from the resulting product ion spectrum. With this information, the isotopic clusters of the protonated trimers of random and block copolymers containing 27% of the d_0-(nominally *R*) and 74% d_2-(nominally *S* isomer) were simulated. [Note that, in this paper, the d_2-compound is to be understood to be only nominally S and the d_0-compound nominally R, and vice versa; neither compound is chemically or isotopically pure.] Comparison of these data with the experimental mass spectra leads to the conclusion that the monomers are randomly distributed in both copolymers. This information, in combination with the optical activity information, given elsewhere, indicates that blocks of each copolymer take the preferred helical sense of the majority enantiomer and that the minority species is simply inserted, randomly, into the helix of the majority enantiomer.

Experimental Section

Deuterium incorporation was achieved by reacting tris-(triphenylphosphine)rhodium chloride (0.2 g) with (*S*)-(−)-β-citronellol (5.33 g), in 40 mL of benzene and 5 mL of ethanol in a 100-mL high-pressure reactor. Deuterium gas was flushed through the system three times before filling the reactor to 100 psi. This pressure was maintained at 60 °C for 48 h. Silica gel was used to remove the catalyst, and the reduction product was distilled at 77 °C under a pressure of 2 Torr.

Mass spectra and tandem mass spectra were recorded using a Finnigan triple-stage quadrupole (TSQ) 700 mass spectrometer (Finnigan MAT, San Jose, CA). Homo- and copolymer samples were prepared for mass spectral analysis by dissolution in hexane at a concentration of approximately 0.5 mg/mL. One microliter (ca. 5×10^{-7} g) of the resulting solution was placed on the rhenium wire filament of a direct evaporation probe and allowed to dry. The probe was introduced into the chemical ionization source of the instrument, and the direct evaporation filament was resistively heated at an initial rate of 100 °C/s and then held at 400 °C while acquiring data. It was then stepped to 1200 °C to pyrolyze any remaining material. Ammonia was used as the reagent gas to produce abundant protonated trimers from all samples. Mass spectra were recorded for the full evaporation period, typically 20 s.

Collisional activation of mass-selected ions was achieved in the tandem experiment with 20-eV collisions on an argon target gas at a nominal pressure of 0.5 mTorr. To measure the isotope distribution of monomers, the resolution of quadrupole 1 was degraded to allow the mass selection of all isotopic

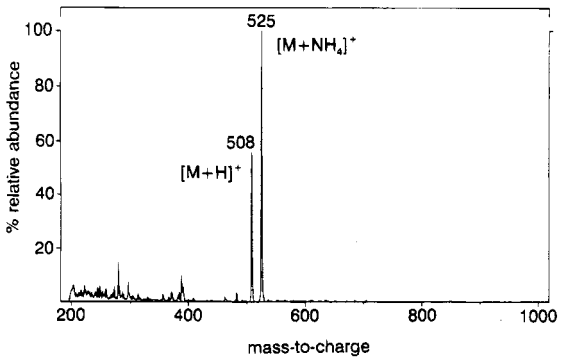

Figure 1. Positive ion desorption chemical ionization mass spectrum of poly((*R*)-2,6−dimethylheptyl isocyanate).

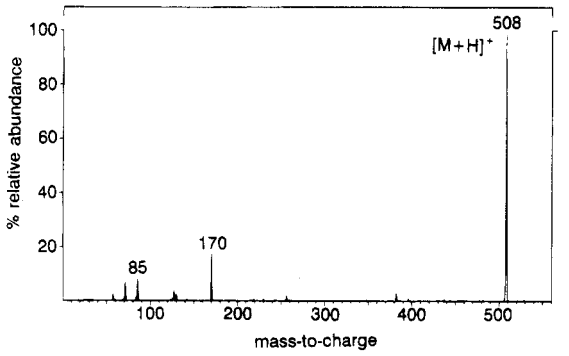

Figure 2. MS/MS product ion spectrum of the protonated (*R*)-trimer.

forms of protonated trimers produced from pyrolysis of the polymers, thereby generating a true isotope distribution of the protonated monomer ions, upon collision-induced dissociation of the trimers.

The copolymers were prepared by the sodium cyanide method in dimethylformamide[1,43] and by an adapted method.[44] The percentages of each monomer used in the production of copolymers **I** and **II** were determined by optical activity measurements. Because the mass spectrometer can only differentiate enantiomers based on deuterium incorporation, it is assumed that all d_0 material is representative of the (*R*)-enantiomer and all d_2 material is representative of the (*S*)-enantiomer. For the mass spectrometric determination of copolymer microstructure, copolymer **I** contains 27.0% d_0-(nominally *R*) and 73.0% d_2-(nominally *S*), while copolymer **II** contains 74.0% d_0-(nominally *R*) and 26.0% d_2-(nominally *S*). The justification for this assumption is discussed herein.

Results and Discussion

Homopolymers generated from (*R*)-2,6-dimethylheptyl-d_0 and (*S*)-2,6-dimethylheptyl-d_2 isocyanate were characterized by DCI-MS and DCI-MS/MS. The DCI mass spectrum of the (*R*)-homopolymer is shown in Figure 1. In the mass range of 200 to 1000 Da, the most prominent features are peaks corresponding to the protonated and ammoniated trimers. The formation of a trimer, first noted by Shashoua,[1] is well suited for the determination of the monomer distribution because it allows the sampling of small sections of the polymer which reveals the local distribution of monomers. The product ion spectrum of the mass-selected protonated trimer of the (*R*)-enantiomer is shown in Figure 2. The most abundant product ion is that due to the protonated monomer at m/z 170. In addition, there is a series of ions at m/z 85, 71, and 57; each consecutive peak is separated by 14 Da, indicating that these are fragment ions of the hydrocarbon substituent.

The mass spectrum of the (*S*)-enantiomer (Figure 3) shows a cluster of isotopes which represent the protonated trimer. As a result of the isotopic labeling of the monomer, the protonated trimer appears at m/z 514 (the base peak in the cluster) rather than m/z 508. However, the incorporation of numbers of deuterons other than two per monomer also occurs to a significant extent and the origins of these peaks must be determined. This was achieved by tandem mass spectrometry. The entire cluster of peaks representing the isotopic region of the protonated (*S*)-trimer was mass-selected by opening the resolution of quadrupole 1. After passing the cluster through the second quadrupole with no collision gas present, the relative abundances of each peak in the *mass-selected* trimer were then recorded operating the third quadrupole at unit resolution. Relative abundances of the same isotopic cluster were separately analyzed, at unit resolution, by simply scanning the third quadrupole with no mass selection in quadrupole 1. Comparison of the relative abundances of the peaks in the trimer region observed in the single-stage mass spectrum to the relative abundances observed in the mass-selected spectrum verified that little or no distortion of the isotope ratios occurred during the mass selection of the cluster of peaks representing the trimer. The relative abundances of all peaks in the MS/MS spectrum from m/z 508 to 520 were found to deviate by less than 7% and to have an average deviation of 2.7% from the relative abundances of the corresponding peaks in the mass spectrum.

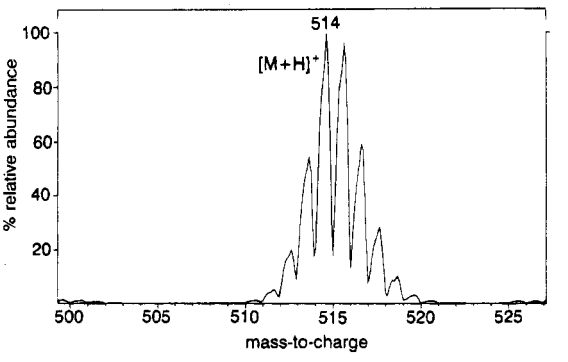

Figure 3. Positive ion desorption chemical ionization mass spectrum showing the isotopic cluster of peaks which represent the protonated trimer of the (*S*)-enantiomer.

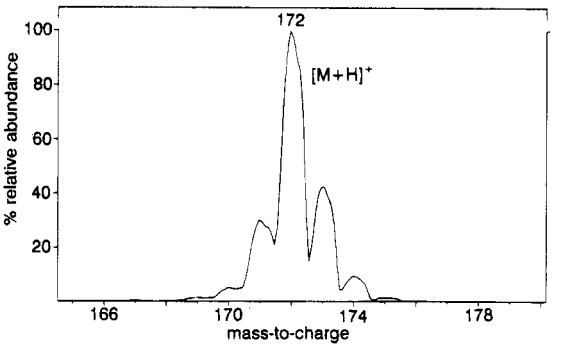

Figure 4. Tandem mass spectrum showing the isotopic distribution of the protonated (*S*)-monomer produced by mass selection and collision-induced dissociation of all isotopic forms of the (*S*)-trimer.

Figure 4 shows the isotopic distribution of the protonated (*S*)-monomer (nominally the d_2-compound) generated by collisional activation after opened-resolution selection of the precursor trimers. These data reveal the average deuterium content of the (*S*)-monomer. It is evident from this spectrum that some (*S*)-monomers contain 0, 1, and 2 deuterons. Comparison of this experimental isotopic distribution with the theoretical

distribution for a compound with molecular formula $C_{10}H_{18}D_2NO$, where the relative abundance of the isotope containing one ^{13}C atom is 11.4% and the relative abundance of the isotope containing two ^{13}C atoms is 0.8%, leads to the conclusion that some (*S*)-monomers also contain 3 and 4 deuterons. By contrast, an analogous opened-resolution experiment performed with the (*R*)-enantiomer showed that the measured isotope ratios for *m/z* 170, 171, and 172 were each within 2% relative abundance of the theoretical isotope ratios of a compound with the molecular formula $C_{10}H_{10}NO$. After accounting for the ^{13}C contribution to each peak and recognizing from the corresponding data for the unlabeled (*R*)-trimer that negligible hydrogen atom loss occurs from the protonated monomer product ion, the percentages of (*S*)-enantiomer containing 0, 1, 2, 3, and 4 deuterium atoms were determined to be 3.3, 17.3, 57.3, 18.8, and 3.3%, respectively.

To check these experimental results, the isotopic cluster representing the trimer was simulated using the relative abundances measured for the (*S*)-monomer in the open resolution experiment. Each peak from *m/z* 508−520 was found to deviate less than 8.4%, with an average deviation of 3.5% from the authentic mass spectrum of the (*S*)-trimer. It is important to measure the deuterium incorporation into the (*S*)-monomer from an MS/MS rather than a mass spectrum. The added specificity provided in the MS/MS experiment ensures that the peaks in the range *m/z* 170−175 are indeed peaks of the monomer generated directly from the dissociation of the trimer and are not all or partially comprised of background ions or ions due to other unknown species. This point is augmented by the fact that, under the experimental conditions used here, ammonia DCI of the enantiomeric 2,6-dimethylheptyl isocyanates produces a monomer peak in the single-stage mass spectrum with a signal-to-noise ratio so poor that the isotope ratios cannot be determined.

From the data in Figures 1 and 3, it is apparent that a random distribution of monomers in copolymers **I** and **II** would result in a trimer with an envelope of peaks from *m/z* 508 to 520, with the center of the envelope determined by the percentage of d_0- and d_2-monomers (viz. (*R*)- and (*S*)-enantiomers) in the average trimer. Conversely, a block polymer (provided the number of monomers per block is significantly greater than three) would be represented by two separate envelopes of peaks, one with a maximum at *m/z* 508 and the other with a maximum at *m/z* 514. A block distribution of monomers is expected to give a spectrum similar to that shown in Figure 5. This mass spectrum was generated from a physical mixture of the (*R*)- and (*S*)-homopolymers in a mole ratio of approximately 1:1.5. Two separate clusters of peaks are observed, with the maximum of the first cluster at *m/z* 508 and the maximum of the second at *m/z* 514, as expected.

Copolymers **I** and **II** were then characterized by DCI-MS. Figure 6a shows the mass spectrum of copolymer **I** which is compared with the simulated isotope distribution for a random copolymer shown in Figure 6b. This latter spectrum was simulated by first determining the isotope ratios of the four possible types of trimers. The molecular ion region of a trimer containing three (*R*)-enantiomers was calculated from the known isotopic abundances for a compound with molecular formula $C_{30}H_{58}N_3O_3$; this agrees with the experimentally observed isotopic distribution for the homotrimer to within 2% relative abundance. The isotope distributions of a

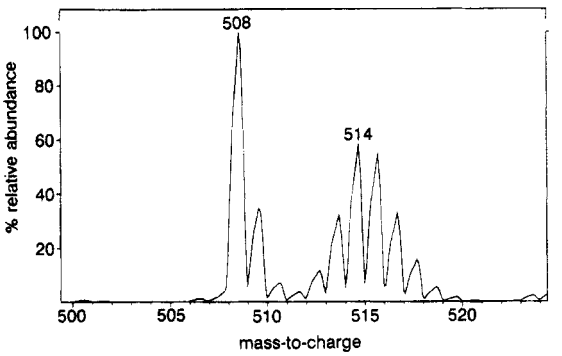

Figure 5. Positive ion chemical ionization mass spectrum showing the protonated trimers generated from a physical mixture of an approximately 1:1.5 ratio of the homopolymers of the 2,6-dimethylheptyl-d_0 (*R*)- and (*S*)-dimethylheptyl-d_2 isocyanate.

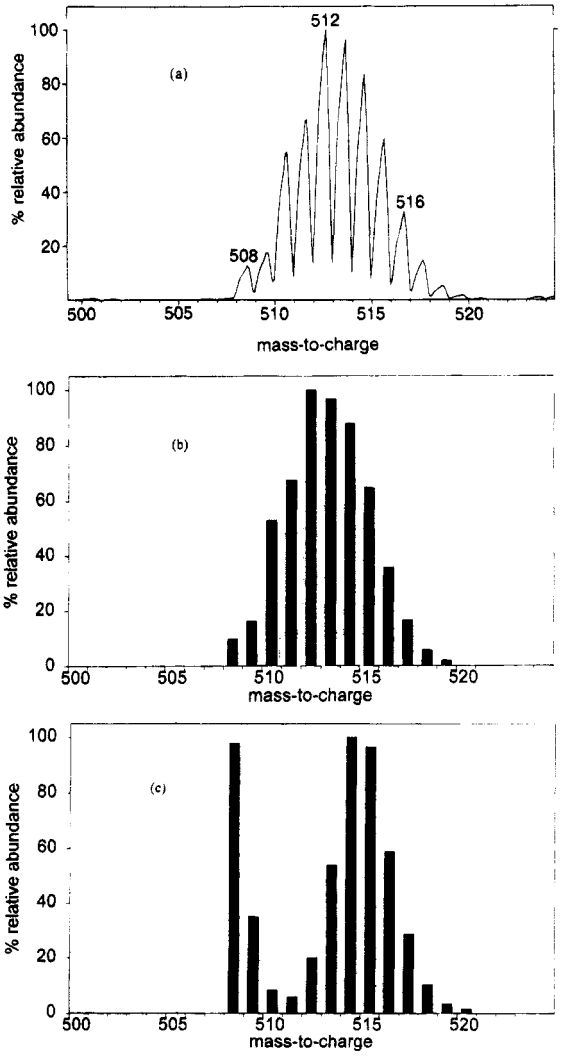

Figure 6. (a) Positive ion mass spectrum of the copolymer comprised of 27% d_0-(*R*) and 73% d_2-(*S*). (b) Simulated copolymer with a random distribution of 27% d_0-(*R*) and 73% d_2-(*S*). (c) Simulated copolymer with a block distribution of 27% d_0-(*R*) and 73% d_2-(*S*).

trimer containing one (*R*)- and two (*S*)-enantiomers and of a trimer containing two (*S*)- and one (*R*)-enantiomers were calculated based on the theoretical ^{13}C isotope content and the measured isotope distribution of the (*S*)-monomer. Finally, the molecular ion region of the trimer containing three (*S*)-enantiomers was measured from the mass spectrum of the (*S*)-homopolymer. The probability of finding each of the given trimers was then

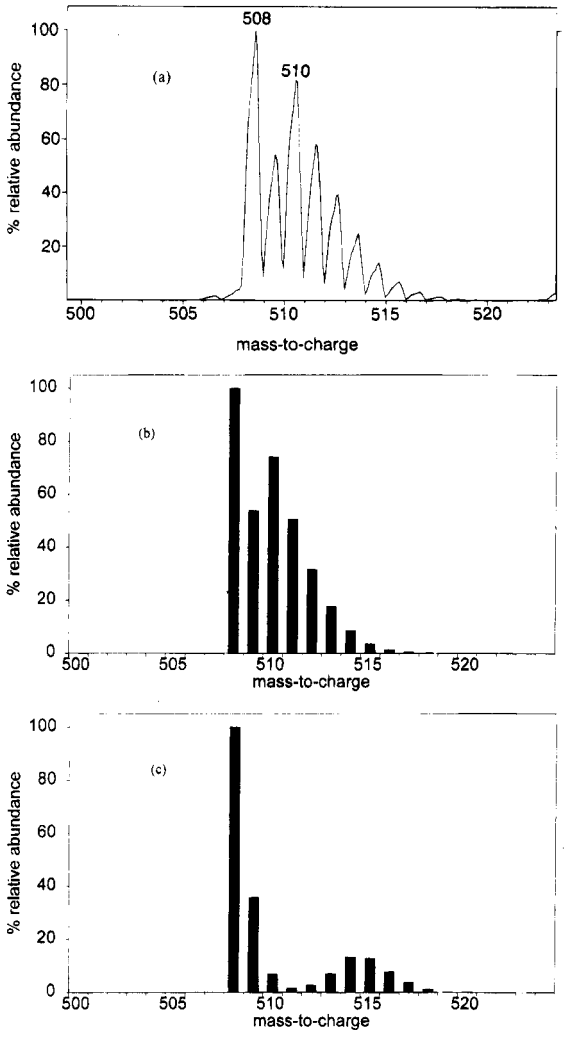

Figure 7. (a) Positive ion mass spectrum of the copolymer comprised of 74% d_0-(*R*) and 26% d_2-(*S*). (b) Simulated copolymer with a random distribution of 74% d_0-(*R*) and 26% d_2-(*S*). (c) Simulated copolymer with a block distribution of 74% d_0-(*R*) and 26% d_2-(*S*).

calculated based on a random, or Bernoullian, distribution of monomers. The entire molecular ion region was then assembled by combining the trimers in the percent probability with which each is expected to be observed on purely random grounds. Statistical methods for the determination of polymer distribution are described in detail elsewhere.[35-37]

The relative abundances of the peaks simulated for a random distribution in copolymer **I** from *m*/*z* 508–519 differ by less than 5.1% from the actual mass spectrum, with an average deviation of 1.9% relative abundance. Figure 6c is the simulated isotope distribution for a block polymer. This was simulated assuming that only two types of trimers are possible, those containing three (*R*)-enantiomers those containing three (*S*)-enantiomers. Clearly, these data show that the monomers are randomly distributed in copolymer **I**. It is unlikely that randomization of the monomer units occurs during the course of DCI because very little of the monomer is observed in the mass spectrum of copolymer **I**; further arguments against this process are given elsewhere for other alkyl isocyanates by the observation that a physical mixture of the two homopolymers does not produce mixed trimer ions.[34]

In Figure 7a–c, analogous data are presented for copolymer **II**. The mass spectrum in Figure 7a closely matches the simulated random distribution in Figure 7b. The relative abundances of all peaks differ by less than 7.8%, with an average deviation of 3.5%. The simulated block distribution in Figure 7c is vastly different from the spectra shown in parts a and b of Figure 7. This leads to the conclusion that the monomer units are also randomly distributed in copolymer **II**.

Isotopic clusters of the trimers of copolymers **I** and **II** were mass-selected using open-resolution collisional activation in an experiment similar to that described for the homopolymers of the (*R*)- and (*S*)-enantiomers to demonstrate the measurement of percent monomer incorporation into each copolymer. Copolymer **I** was mass selected with little distortion compared to the single-stage mass spectrum; each peak had a deviation of less than 2.6% and an average deviation of 1.3%, in the mass range from *m*/*z* 508 to 519. The monomer observed in the product ion spectrum has a composition of 32.8% d_0, assigned as the (*R*)-isomer and 67.2% d_2, assigned as the (*S*)-isomer; the optical experiments provide a composition of 27.0% (*R*)-isomer (sum of the entries for d_0-(*S*) and d_0-(*R*) in Table 1) and 73.0% for the (*S*)-isomer (sum of the entries for d_2-(*S*) and d_2-(*R*) in Table 1). The ions comprising copolymer **II** were mass-selected as a group, each with a deviation of less than 7.5% relative abundance and an average deviation of 2.0% abundance relative to the ion abundances in the single-stage mass spectrum in the mass range from *m*/*z* 508 to 519. The average monomer produced from this copolymer had a composition of 74.6% d_0, assigned to the (*R*)-isomer, and 25.4% d_2, assigned to the (*S*)-isomer, compared to 74.0% for the (*R*)-isomer (sum of the entries for d_2-(*R*) and d_0-(*R*) in Table 1) and 26.0% for the (*S*)-isomer (sum of the entries for d_2-(*S*) and d_0-(*S*) in Table 1) as determined by optical rotation.

Possible sources of error in the mass spectrometric determination of the monomer distribution include different rates of pyrolysis and fragmentation of each enantiomer. However, these are minimized because the (*S*)- and (*R*)-enantiomers are differentiated only by isotopic substitution at a site remote from the chiral C-2 carbon. Determination of the degree of deuterium incorporation in the (*S*)-enantiomer by collision-induced dissociation of the entire molecular ion region may be in error by a few percent. Also, the reported percentages of the d_0-(*R*) and d_2-(*S*) enantiomers used to prepare the copolymers may contain a small error. Each of these errors contribute to the minor differences observed between the simulated random copolymers and mass spectra of the same copolymers. The agreement observed between the simulated and the experimental data is taken not only as evidence for random monomer distributions but also as a justification for the procedure, used here, of following the behavior of the (*S*)-enanti-

Table 1. Percentages of (*R*)- and (*S*)-Enantiomeric Monomers Used To Prepare Copolymers I and II[a]

monomer unit	copolymer **I** (%)	copolymer **II** (%)	monomer unit	copolymer **I** (%)	copolymer **II** (%)
d_2-(*S*)	67.2	23.9	d_2-(*R*)	5.8	2.1
d_0-(*S*)	0.8	2.2	d_0-(*R*)	26.2	71.8

[a] Monomer enantiomeric excess was determined by optical activity measurements on the individual compounds. The copolymer compositions were determined by weighing the mirror-image monomers and conducting the polymerization as usual.[43,44]

omer by deuterium incorporation, though this was not achieved quantitatively.

There are two possible conformational arrangements of the enantiomeric copolymers, now known to be comprised of randomly distributed monomers. In one, the enantiomer in excess, the majority enantiomer, determines the helical conformation, and the minority enantiomer adopts this helical sense. The other possibility is that each enantiomer takes its preferred helical conformation, in which case helix reversals are required to follow the numerous microstructural changes from (*R*) to (*S*) and vice versa. In work to follow, it will be shown how the mass spectrometric data allow the use of optical activity and empirical force field calculations (EFF) to show that the copolymers follow the preferred helical sense of the majority enantiomer, with the minority enantiomer adapting to this helix.[14] These mass spectrometric data also show that the chiral bias of each monomer toward one helical sense does not act to perpetuate monomer selection in the synthesis.

Conclusions

Copolymer microstructure of alkyl isocyanates comprised of enantiomeric monomers is determined by desorption chemical ionization mass spectrometry with the aid of enantiomeric specific deuteration. The distribution of the monomers in two copolymers generated from (*R*)-2,6−dimethylheptyl isocyanate and (*S*)-2,6-dimethyl-5,6-dideuteroheptyl isocyanate was determined to be random. This was done by an unusual mass spectral technique which used open-resolution product ion (MS/MS) scans. This allowed (i) the determination of the average degree of deuterium incorporation into the average monomer of a homopolymer by dissociation of all isotopic forms of the trimer and (ii) determination of the ratio of labeled to unlabeled monomer used to produce a copolymer, again by simultaneous dissociation of all isotopic forms of the trimer. These results, in addition to empirical force field calculations and optical rotation and circular dichroism spectra to be published,[14] lead to the conclusion that the majority enantiomer controls the helical conformation of the copolymer. This is the first microstructural analysis of D,L-copolymers, although the random result is implicit in earlier results for D- and L-leucine copolymers.[45] The mass spectrometric techniques described here appear to be applicable to a wide range of polymers.

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