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Near-Infrared Spectroscopic Analyses of Poly(ether urethane urea) Block Copolymers.

Part I: Bulk Composition

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The ability of near-infrared (NIR) diffuse reflectance spectroscopy to perform rapid bulk composition analyses of poly(ether urethane urea) (PEUU) block copolymers is demonstrated. Six polymer samples with known elemental compositions were used to construct calibration models using the method of classical least-squares (CLS). Results indicate that NIR diffuse reflectance spectroscopy can determine hard-segment and soft-segment contents of the bulk polymers within 2.6% mass over a range of 31% mass. Errors in the calibrations were caused by nonrepresentative NIR sampling of the polymers and by the presence of side products in the polymers. NIR spectra of model hard- and soft-segment materials are used to assign NIR bands to specific functional groups in the polymers.

Index Headings: Near-infrared spectroscopy; Polymers.

INTRODUCTION

Segmented poly(ether urethane urea) (PEUU) copolymers, which are composed of alternating hard- and soft-segment blocks, are commercially useful materials with interesting properties worthy of fundamental investigation.¹⁻⁶ The polyether soft segment provides flexibility and elasticity to the polymer. The hard segment, generally comprised of the reaction products of a diisocyanate and a low-molecular-weight diamine, can noncovalently self-associate to form domains that act as effective crosslinks and reinforce the polymers. The physical properties of these polymers greatly depend on the composition and the degree of phase separation.

Some physical properties of segmented PEUU copolymers can be measured directly by mechanical analyses.^{3,5,6} Other methods, such as thermal analysis,^{2,5,6} x-ray scattering,² x-ray photoelectron spectroscopy,⁴ and FT-IR spectroscopy,³ also provide valuable information that can be used to probe composition and morphology. These techniques are useful for polymer analysis, but require specific and careful sample preparation, leading to long analysis times. For those situations where a rapid determination of chemical composition of polymers is required, near-infrared (NIR) spectroscopy can be valuable.^{7,8}

NIR spectra contain vibrational overtone and combination bands from C-H, N-H, O-H, and C=O groups. Quantitative NIR polymer analysis depends on the sensitivity of NIR spectra to the relative amounts and struc-

tural states of functional groups in the polymer. Earlier NIR determinations of octane numbers in gasolines,⁹ functional groups in hydrocarbons,¹⁰ and ethylene and propylene contents in EPDM terpolymers¹¹ illustrate the ability of NIR spectroscopy to determine important compositional and structural properties.

Because the absorptivities of overtone and combination bands in the NIR region are much lower than the absorptivities of fundamental bands in the infrared region, thicker and bulkier samples can be analyzed with NIR spectroscopy than with IR spectroscopy. As a result of these less stringent sample preparation requirements, NIR analysis is more rapid than IR analysis. In past years, successful NIR analyses of bulk agricultural products have been made.⁷ In the same way, NIR spectroscopy can be used to study bulk polymers.

NIR spectral features of different analytes, such as hard and soft segments, in a polymer are generally highly overlapped. Therefore, multivariate calibration methods are usually necessary for quantitative NIR work.^{7,12-14} Examples of these methods are partial least-squares (PLS),¹¹⁻¹³ classical least-squares (CLS),^{11,14} and principal component regression (PCR).¹³ These methods can use all available spectral frequencies for quantitative analysis, and can thus provide accurate analyses for analytes with highly overlapped spectral features. Earlier application of the PLS and CLS methods with NIR polymer analysis resulted in accurate composition determinations.¹¹

In the CLS method, the relationship between spectral absorbances and analyte concentrations is assumed to follow the Beer-Lambert law.^{11,14} In the calibration phase of CLS, basis spectra that represent each pure component in the polymer are determined with the use of the spectra of calibration standards with known analyte concentrations. To determine calibration fit, the basis spectra are fit by the least-squares method to the spectra of each of the calibration standards. The coefficients of this fit are equal to the calibration estimates of analyte concentrations in the standards.

The major difficulty with NIR spectroscopy of bulk polymers is the nonreproducible sampling of the polymer, which leads to the presence of multiplicative effects and baseline shifts in the spectra.¹¹ These effects are especially large if the bulk samples are highly scattering like the PEUU samples used in this work. In order to construct a CLS calibration from NIR spectra of bulk PEUU samples, the calibration spectra must be corrected for these effects before calibration. The method of multiplicative scatter correction (MSC) has been used

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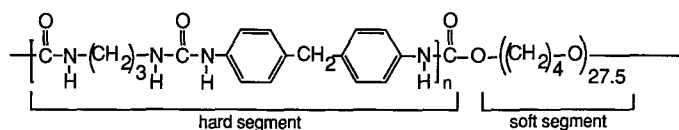


FIG. 1. Chemical structure of PEUU copolymers.

in other applications to reduce these effects and improve calibration results.^{15,16}

After a CLS calibration is prepared, prediction of analyte concentrations can be made with the use of spectra with unknown multiplicative effects and baseline shifts.^{11,14} As a result, the CLS method is suitable for situations where sampling speed is a high priority and sample preparation is minimal. In this work, the CLS method will be used to construct calibrations for hard-segment and soft-segment concentrations in PEUU copolymers.

EXPERIMENTAL

Materials. PEUU polymers were synthesized from 4,4'-methylenebis(phenylene isocyanate) (MDI) (Upjohn Company), hydroxy-terminated poly(tetramethylene oxide) of approximately 2000 g/mol (PTMO-2000) (Quaker Oats Co.), and 1,3-propylenediamine (PD) (Aldrich). MDI and dimethylacetamide (DMA) (Burdick and Jackson Lab. Inc.) were vacuum-distilled. MDI was refrigerated until needed. PD was distilled under an argon blanket. PTMO-2000 was dried in a vacuum oven for 24 h at 60°C. Dibutyltin dilaurate (ICN Pharmaceuticals, Inc.) was used as received.

Synthesis. A two-step solution synthesis was used for the PEUU samples from MDI, PD and PTMO-2000. Synthesis of the 2:1:1 polymer will be described in detail as being representative of the procedure for the series. The 2:1:1 refers to the mole ratio of MDI to PD to PTMO-2000, respectively. A 3-necked 250-mL round-bottom flask was set up with a mechanical stirrer, pressure-equalizing dropping funnel, and argon inlet. For removal of moisture, the glassware was flamed-out under argon. To MDI (4.14 g, 16.5 mmol) dissolved in DMA at room temperature, a solution of PTMO-2000 (16.55 g, 8.28 mmol) and 2 drops of catalyst were added. The solution concentration was 10–15% w/v. The temperature was slowly raised to 60°C and maintained for 1 h. After cooling back to room temperature, the dropping funnel was charged with a 5% solution of the diamine (0.614 g, 8.28 mmol), which was then added dropwise with rapid stirring. In all cases, the solution thickened considerably after about 80% of the diamine had been added, so that more DMA had to be added to facilitate uniform mixing. After complete addition, the temperature was again raised to 60°C for about four additional hours. The product was then separated by precipitation into 600-mL methanol, filtered, rinsed five times in methanol, and vacuum dried at 80°C for 12 h. Additionally, to ensure more complete removal of low-molecular-weight products, the polymers were redissolved in DMA and reprecipitated in methanol. The basic structure of the polymers after an ideal reaction is shown in Fig. 1.

A hard-segment model compound was prepared by reaction of a 1:1 molar mixture of MDI and PD. Pure PTMO-2000 was used as a soft-segment model. Six PEUU

TABLE I. Bulk elemental compositions of PEUU samples.

Sample name	Mass percent nitrogen	Mass percent hard segment	Mass percent soft segment
1:0:1	1.27	11.3	88.7
2:1:1	2.25	16.8	83.2
3:2:1	4.16	27.4	72.6
4:3:1	5.36	34.0	66.0
5:4:1	6.25	38.9	61.1
6:5:1	6.89	42.5	57.5

polymers were prepared with the use of reaction stoichiometries of 1:0:1, 2:1:1, 3:2:1, 4:3:1, 5:4:1, and 6:5:1 (MDI:PD:PTMO-2000); these polymers were used as calibration samples. The percent (mass) of nitrogen in the six polymers, determined from elemental analysis (Huffman Laboratories, Golden, CO), is shown in Table I. The mass percent hard-segment value for each sample was obtained from the percent nitrogen value as follows: a calibration curve of mass percent hard segment vs. mass percent nitrogen for an ideal reaction was constructed, and this curve was used to determine experimental mass percent hard-segment values from experimental mass percent nitrogen values. The percent soft-segment value was determined as 100 minus the mass percent hard-segment value. It should be noted that this method of determining hard- and soft-segment contents does not take into account the formation of side products in the polymers.

NIR Bulk Polymer Analysis. The PEUU samples were analyzed in the form that they took immediately after synthesis and purification. The different polymer samples had different physical appearances and consistencies (e.g., fibrous, powdery). Each sample was packed in a sampling cup with a quartz window and was subsequently analyzed by the spectrometer.

The near-infrared reflectance spectra of the six calibration samples, the hard-segment model, and the soft-segment model were obtained with a Technicon InfraAlyzer 500C near-infrared reflectance spectrometer. The spectral range was 1100 to 2200 nm; the region 1350 to 1450 nm was deleted because of instrumental anomalies. The wavelength accuracy was ± 1 nm, and the nominal resolution was 10 nm. Four spectra of each sample were obtained—one spectrum each, with the specimen in four different orientations in the spectrometer. Each individual scan lasted 1.5 min. In some cases, second-derivative spectra were used for calibration (Technicon IDAS software, Tarrytown, NY).

Data Analysis—Bulk Polymers. CLS calibrations were constructed from both $\log(1/\text{reflectance})$ and second-derivative $\log(1/\text{reflectance})$ NIR spectra of the bulk polymers. In each case, the method of multiplicative scatter correction (MSC) was used to correct the spectra for multiplicative and baseline effects before CLS calibration.^{15,16} Replicate samples were treated separately in the

TABLE II. CLS calibration results.

Spectral correction	Calibration SEE for mass % hard segment
None	2.6
Second derivative	2.5

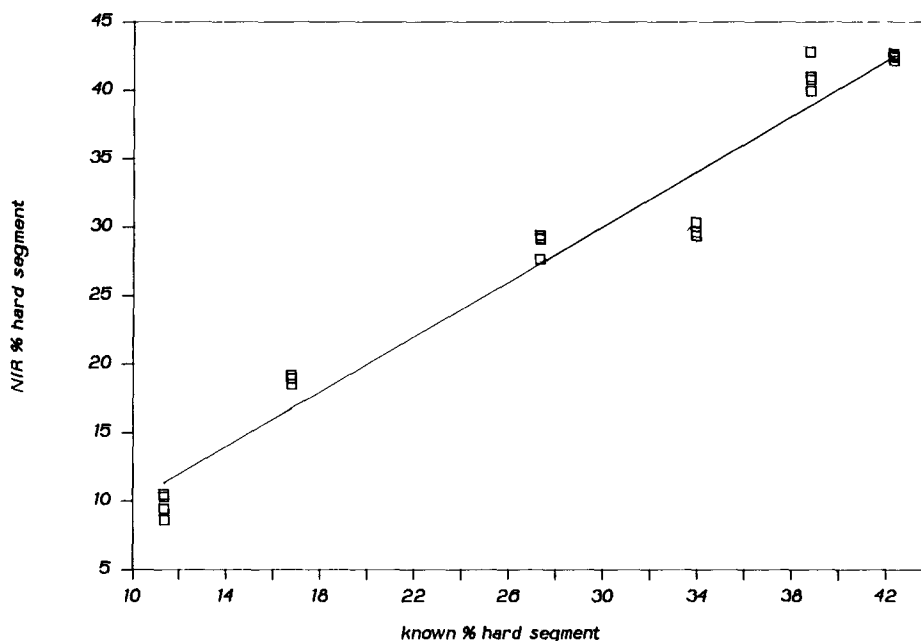


FIG. 2. Calibration curve for CLS calibration for percent hard segment that uses second-derivative NIR spectra.

calibration procedure. All calibrations were evaluated according to the standard error of estimate (SEE) value:

$$SEE = \sqrt{\frac{\sum_{j=1}^{NC} (\bar{C}_{i,j} - C_{i,j})^2}{NC}} \quad (1)$$

where $C_{i,j}$ is the known concentration of analyte i in sample j , $\bar{C}_{i,j}$ is the predicted concentration of analyte i in sample j , and NC is the number of calibration samples.

RESULTS AND DISCUSSION

Calibration Results. The SEE values for CLS calibrations for percent hard segment and percent soft segment in the PEUU copolymers are listed in Table II. They indicate that the NIR spectroscopic method can determine bulk composition within 2.6% mass over a range of 31% mass. Slightly better results are obtained if second-derivative spectra are used, because sampling effects are reduced and spectral resolution is improved. Because percent hard- and soft-segment values are inversely proportional, calibration errors for both quantities are equal for a given analysis. These calibration results are encouraging, because they indicate that rapid, accurate analyses of bulk polymers can be performed.

In order to further assess the ability of NIR spectroscopy to perform bulk polymer analyses, the sources of errors in the calibrations were investigated. Calibration errors can be caused by errors in the spectral data or by errors in the elemental analysis data for the polymers. Errors in the spectral data might arise from nonlinear absorbances, instrumental anomalies, or inadequate removal of sampling effects by MSC. Errors in the reference hard- and soft-segment concentration data might result from random errors in elemental analysis results. However, systematic errors in the reference hard- and soft-segment concentrations might result from the pres-

ence of side products in the polymers, which is not accounted for in the determination of hard- and soft-segment concentrations from percent nitrogen data.

The calibration curve for percent hard segment that used second-derivative spectra is shown in Fig. 2. Note that the points that correspond to replicate samples fall into tightly bound clusters with deviations of approximately 1 to 3% mass, which are similar to or lower than the overall calibration error of 2.5% (see Table I). This result indicates that sampling errors, caused by a combination of baseline shifts, multiplicative spectral effects, and sample nonhomogeneity, contribute only a fraction to the calibration error. It should also be noted that the calibration error is not distributed equally over all of the samples. The clusters for the 4:3:1 and 5:4:1 samples are located far from the calibration line, but the other clusters are close to the line. This result indicates the presence of two possible error sources in the calibration: (1) nonrepresentative sampling of the 4:3:1 and 5:4:1 samples, or (2) the presence of unexpected side products in these samples. It is unlikely that differences in phase separation of these samples are responsible for the error, because the effect of phase separation on the NIR spectra of these polymers is small.¹⁷

The sources of error in the CLS calibrations can be investigated by comparison of CLS-estimated spectra of the hard and soft segments in the polymer with spectra of hard- and soft-segment model compounds. If nonrepresentative sampling is the source of the calibration error, systematic errors in the CLS-estimated spectra will be present. These errors are indicated by the presence of bands from groups in the hard segment in the CLS-estimated soft-segment spectrum, and vice versa. If the presence of side products is the source of the calibration error, spectral features from the side products, not present in the spectra of the model compounds, will be present in the CLS-estimated spectra. Furthermore, if it is assumed that side product formation primarily affects urea and urethane groups in the polymers, only the re-

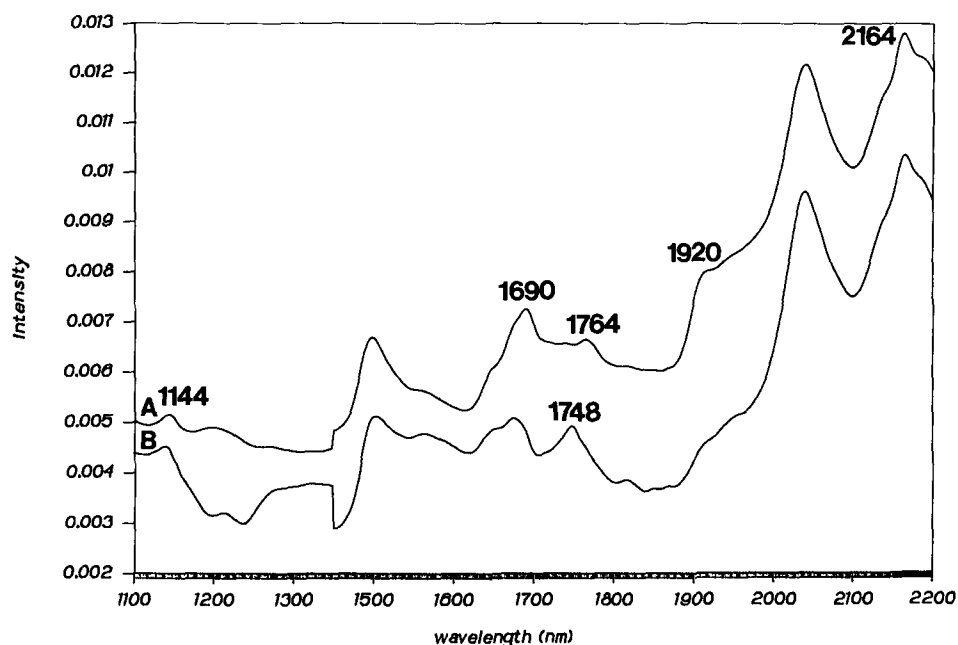


FIG. 3. NIR diffuse reflectance spectrum of the hard-segment model polymer (A), and the CLS-estimated spectrum of the hard segment in PEUU copolymer (B).

gions of carbonyl and N-H absorption (1450–1600 nm and 1900–2100 nm)^{7,18,19} will be affected by side product formation.

Figures 3 and 4 show the CLS-estimated spectrum and model compound spectrum for the hard segment and soft segment, respectively. Comparison of the estimated spectrum of the hard segment in the polymer (Fig. 3B) and the hard-segment model spectrum (Fig. 3A) reveals significant differences in the C-H stretching overtone region (1650–1800 nm) and the N-H and carbonyl absorption region (1900–2100 nm). The band at 1748 nm in the estimated hard-segment spectrum, which is at the same position as a band in the soft-segment model spec-

trum (Fig. 4A), indicates the occurrence of nonrepresentative sampling. In the carbonyl and N-H region (1900–2100 nm), a shoulder at 1920 nm in the hard-segment model spectrum (Fig. 3A) is not present in the estimated hard-segment spectrum (Fig. 3B). Although this difference might be caused by a difference in the morphology of the hard-segment model and the hard segment in the polymers, it might also indicate the presence of side products in the polymers.

The estimated soft-segment spectrum (Fig. 4B) and soft-segment model spectrum (Fig. 4A) are very similar. However, the band at 2160 nm in the estimated soft-segment spectrum, which is in approximately the same

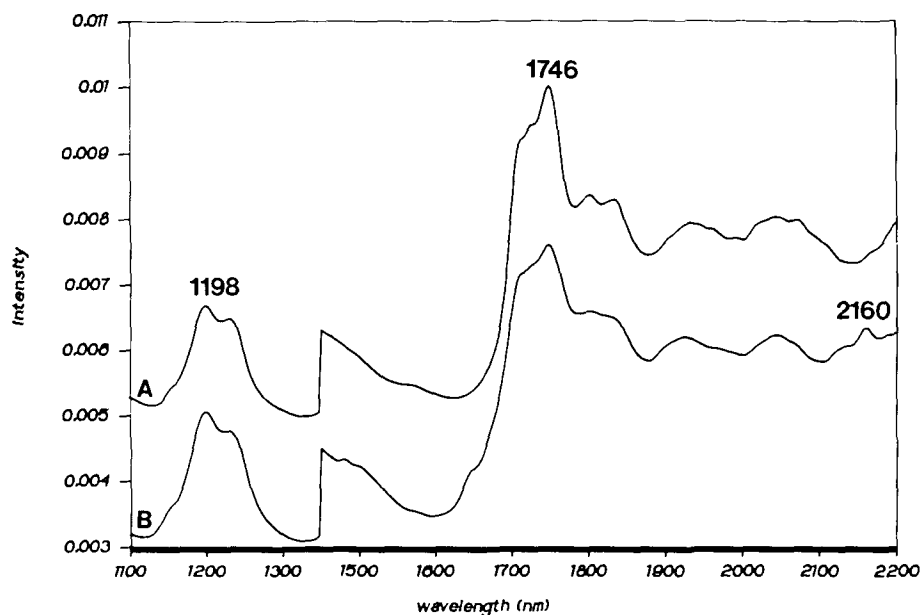


FIG. 4. NIR diffuse reflectance spectrum of the soft-segment model polymer (A), and the CLS-estimated spectrum of the soft segment in PEUU copolymer (B).

position as the 2164-nm band in the hard-segment model spectrum (Fig. 3A), is a clear indication of nonrepresentative sampling. Other differences between the soft-segment spectra in Fig. 4 might be weaker indicators of nonrepresentative sampling, or results of morphological differences between the soft-segment model and the soft segment in the polymers. In summary, comparison of CLS-estimated spectra and model compound spectra indicates the occurrence of nonrepresentative sampling and, possibly, the presence of side products in the polymers. Additional results from a reference method that measures functional group concentrations (e.g., NMR or IR spectroscopy) might allow identification and determination of side products.

Band Assignments. Although NIR bands are highly overlapped, assignments of NIR absorptions to specific functional groups can be made. NIR bands at 1144, 1690, and 2164 nm in the hard-segment model spectrum (Fig. 3A) correspond to the second-overtone, first-overtone, and combination bands of the aromatic C-H stretch in the MDI unit. These bands are in close proximity to aromatic C-H bands present in the NIR spectra of polystyrene.⁷ The absorbance at 1764 nm, which is in the region of previously observed bands in the NIR spectra of aliphatic hydrocarbons^{7,10} and EPDM terpolymers,¹¹ is from the methylene group in the MDI unit and from methylene groups in the chain extender. Absorbances in the region 1450 to 1600 nm arise from overlapped N-H stretching first-overtone bands and third-overtone carbonyl stretching bands. The region 1900 to 2100 nm also contains contributions from combination N-H stretching and amide bands and from second-overtone carbonyl stretching bands. Absorptions in these regions are observed in NIR spectra of proteins^{7,18} and amino acids.¹⁹ More detailed assignments of absorbances in the region 1900 to 2100 nm are made in the following paper (part II).

The NIR spectrum of the soft-segment model (Fig. 4A) is dominated by methylene stretching overtone bands. The absorbances in the region of 1198 nm are second-overtone methylene stretching bands, and the absorbances at 1746 nm are first-overtone methylene stretching bands. Similar absorbances are observed in spectra of ethylene-propylene rubbers¹¹ and of aliphatic hydrocarbons.^{7,10} Note that these absorbances are not highly overlapped with absorbances from aromatic C-H groups in the hard segment (Fig. 3). As a result, accurate determinations of hard- and soft-segment concentrations are possible.

CONCLUSIONS

This analysis has shown that rapid composition determinations of bulk PEUU polymers can be made with the use of NIR diffuse reflectance spectroscopy. The method of CLS provided accurate calibrations of NIR spectra to hard-segment and soft-segment fractions in the polymers. The observed calibration errors were caused by nonrepresentative NIR sampling of the polymers. It is also possible that the presence of side products in the polymers contributed to the calibration errors. NIR absorbances of specific groups in the polymers were determined from NIR spectra of model compounds.

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