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# Enantiomeric separations using poly(L-valine) and poly(L-leucine) surfactants
## Investigation of steric factors near the chiral center

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**Abstract**

This study examined the effect of steric factors near the stereogenic center on polymerized surfactants, sodium *N*-undecyl-L-leucine, sodium *N*-undecyl-L-norleucine, sodium *N*-undecyl-L-tert.-butyl leucine, sodium *N*-undecyl-L-isoleucine, sodium *N*-undecyl-L-valine, sodium *N*-undecyl-L-norvaline, and sodium *N*-undecyl-L-proline. The effect of steric factors near the chiral center of the polymeric surfactants were examined using binaphthyl derivatives, aminoglutethimide, and 2,2,2-trifluoro-1-(9-anthryl)ethanol. In addition, fluorescence spectroscopy was used to determine the hydrophobicities of these surfactants using the environmentally-sensitive probe pyrene.


*Keywords:* Enantiomer separation; Steric factors; Poly(L-valine); Poly(L-leucine); Surfactants

## 1. Introduction

Electrokinetic chromatography (EKC) is a robust technique for the separation of enantiomers. The strength of EKC for the separation of optically active compounds lies in the variety of pseudo-stationary phases that can be used such as cyclodextrins [1–4], cyclodextrin derivatives [4–6], heparin [7], chiral metal complexes [8–10], macrocyclic antibiotics [11–14] and chiral surfactants [15–18]. Chiral surfactants for enantiomeric separation were first introduced by Terabe et al. in 1989 [18]. Since 1994 our laboratory has been pursuing the development and understanding of polymeric surfactants for use as pseudo-stationary phases in EKC. These materials have certain distinct advantages over normal micelles which have been discussed previously [19].

Recently, a number of publications have investigated polymerized chiral surfactants for the separation of enantiomers [20–23]. Dobashi et al. studied the effect of increasing steric factors of the analyte on enantiomeric selectivity [20]. Work done in our laboratory by Shamsi et al. demonstrated that an improvement in enantiomeric separation was observed with dipeptide surfactants compared to amino acid surfactants for three of the four chiral com-

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pounds tested [21]. Other work performed in our laboratory by Billiot et al. proved that the amino acid order of the dipeptide surfactants has a significant effect on the chiral recognition properties [22]. Our group also developed a technique for determining which amino acid is the primary site of interaction for the analyte [23]. Previously, we reported using polymerized surfactant L-glutamic acid derivatives to determine the effect of steric factors near the stereogenic center on enantiomeric separation [24]. Our work demonstrated that replacing the carboxylic hydrogen on the side chain of glutamic acid with a methyl, ethyl or tert.-butyl group significantly increased the resolution for five out of the six compounds examined. Also, fluorescence studies indicated that amino acid-based polymerized surfactants do not undergo a transition from a more hydrophobic configuration to a lesser hydrophobic configuration with increasing pH [24].

Studies using chiral stationary phases and pseudo-stationary phases have demonstrated the importance of hydrophobic/hydrophilic interactions, electrostatic interactions, π-bonding, hydrogen bonding and steric factors for enantiomeric separations [24–31]. Since the introduction of polymerized surfactants, limited work has been done to understand the effect of steric factors of the selector on enantiomeric separation. Our earlier efforts to address this issue increased the steric factors near the stereogenic center along with increasing the hydrophobicity of the surfactants, while also changing the hydrogen bonding characteristics of the surfactants. Our previous work failed to separate the steric factors of the polymeric surfactants from increasing hydrophobicity. Separation of steric factors from other considerations would allow for better understanding of the impact sterics have on enantiomeric separation. In turn, this could lead to better design of polymeric surfactants for the separation of chiral compounds. The separation of steric considerations from the other interaction mechanisms was achieved by producing a series of polymeric surfactants which contain leucine, nor-leucine, isoleucine, and tert.-leucine. In addition, polymeric surfactants containing proline, valine and nor-valine were also studied. These stereoisomeric polymeric surfactants have similar hydrogen bonding, electrostatic capacity and π-bonding characteristics while possessing different steric factors near the stereogenic center. Using this technique, a systematic investigation of steric effects near the stereogenic center on enantiomeric separation were performed. Fluorescence probe studies using pyrene were also conducted to compare the hydrophobicities of the various surfactants.

Fluorescence probes, particularly pyrene, are used to determine the polarity of micelles and polymerized surfactants in aqueous environments [31–35]. Also, pyrene is almost exclusively solubilized by micelles since it has a low solubility in water [35]. The fluorescence emission spectrum of pyrene using high spectral resolution contains five vibronic bands. The third vibronic band is extremely sensitive to changes in the polarity of the probe's environment [36]. Therefore the (I/III) band ratio is used to measure polarity changes [37]. A decrease in the I/III ratio indicates an increase in hydrophobicity.

## 2. Experimental

### 2.1. Chemicals and reagents

Leucine, nor-leucine, isoleucine, tert.-leucine, proline, valine and nor-valine were purchased from Bachem (Torrance, CA). Undecylic acid and *N*-hydroxysuccinimide were purchased from Sigma (St. Louis, MO). The analytes (±)-1,1′-bi-2-naphthol (BOH) (99%), (±)-1,1′-binaphthyl-2,2′-diamine (BNA) (99%), (±)-1,1′-binaphthyl-2,2′-phosphate (BNP) (99%), (±)-2,2,2-trifluoro-1-(9-anthryl)-ethanol (TFAE), (±)-aminoglutethimide (AG), and pyrene (99+%) were purchased from Aldrich (Milwaukee, WI). All compounds were used as received, unless otherwise stated.

### 2.2. Synthesis of polymers

The monomers of sodium *N*-undecyl-L-leucine (poly-L-SUL), sodium *N*-undecyl-L-norleucine (poly-L-SUNL), sodium *N*-undecyl-L-tert.-butyl leucine (poly-L-SUTBL), sodium *N*-undecyl-L-isoleucine (poly-L-SUIL), sodium *N*-undecyl-L-valine (poly-L-SUV), sodium *N*-undecyl-L-norvaline (poly-L-SUNV), and sodium *N*-undecyl-L-proline (poly-L-SUP) were synthesized according to the procedure described by Wang and Warner [19]. These car-

boxylic acid compounds were then converted into their corresponding sodium salt form by adding an appropriate amount of sodium bicarbonate. The monomers were polymerized at 100 m*M* concentrations by γ-irradiation ($^{60}$Co; 70 krad/h) for about 7 days [19]. After polymerization the NMR spectrum was absent of the vinyl proton signals.

### 2.3. Capillary electrophoresis

The EKC experiments were conducted on a Biofocus 3000 automated CE system (Bio-Rad, Hercules, CA) with a multi-wavelength UV absorbance detector. Separations were performed with uncoated fused-silica capillaries of 50 μm I.D. and 354 μm O.D. purchased from Polymicro Technologies (Phoenix, AZ). A column length of 55 cm was used that provided an effective length of 45.5 cm (to detection window). All separations were performed at a constant voltage of 25 kV.

### 2.4. Fluorescence

Fluorescence emission spectra were acquired on a Spex Model F2T21I Fluorolog-2 spectrofluorometer at ambient temperature. Samples were measured in a 1-cm quartz cell with excitation and emission slits set for a 4.1 nm and 1.7 nm band pass, respectively. Emission spectra of pyrene were collected with an excitation wavelength of 335 nm.

### 2.5. Electrolyte and standard procedure

The background electrolyte for the binaphthyl experiments consisted of 10 m*M* borate and 100 m*M* TRIS pH 10, for TFAE 30 m*M* borate pH 10, and for aminoglutethimide 80 m*M* TRIS pH 9.2. After addition of the surfactant to the buffer solution the pH was readjusted if needed with 1 *M* NaOH or 1 *M* HCl. The samples were then filtered using a 0.45 μm membrane filter. The analytes were prepared using a 50:50 mixture of methanol–water. The analyte concentrations were 0.05 mg/ml for binaphthyl derivatives, 0.1 mg/ml for TFAE and 0.5 mg/ml for AG. The samples were pressure-injected for 2 s. Prior to use, the capillary was conditioned with 1 *M* NaOH for 1 h, 0.1 *M* NaOH for 30 min and triply distilled water for 15 min. The buffer solution was pressured injected for 10 min for final conditioning and filling of the capillary. After each analysis, the capillary was pre-rinsed with the buffer solution for 3 min. The capillary was thermostated with an aqueous coolant at 25 °C for the binaphthyl separations, 15 °C for TFAE and aminoglutethimide separations. Absorption at 280, 254, and 220 nm for the binaphthyls, TFAE, and AG was employed for detection, respectively.

A stock solution of $8.90\times10^{-4}$ *M* pyrene was prepared by dissolving the appropriate amount of pyrene in cyclohexane. The polymer solutions were prepared by dissolving 30 mg in 5 ml of 10 m*M* sodium diphosphate buffer solution pH 7. One hundred microlitres of the pyrene stock solution were pipetted into a 10-ml vial and then dried using a stream of nitrogen. The surfactant solutions were then added to the dried probe sample. The sample was then vortexed and allowed to equilibrate overnight. Before analysis, the samples were purged for 15 min with a stream of nitrogen.

## 3. Results and discussion

### 3.1. Physical characterization

A comparison of the hydrophobicities of these polymeric surfactants was accomplished by using the environmentally-sensitive probe pyrene. As illustrated in Fig. 1, no significant difference in the hydrophobicity of leucine or valine stereoisomers was observed. In fact, there is little variance in the

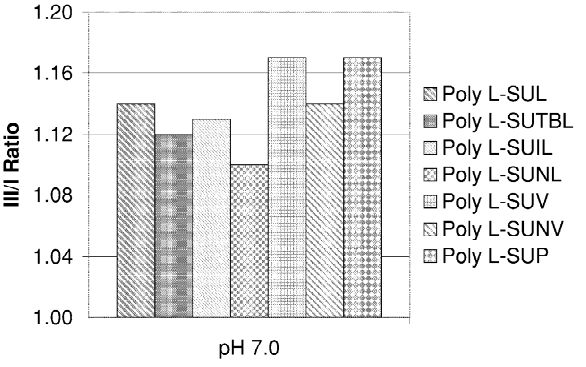


Fig. 1. Bar graph of the III/I ratios of the stereoisomers of leucine, valine, and proline surfactants and pyrene.

hydrophobicity of any of these surfactants (Fig. 1). Since these polymeric surfactants have similar hydrophobicities, differences in enantiomeric separations are attributed to variations in steric factors near the chiral center.

### *3.2. Separations*

The structure of the polymeric surfactants and the chiral analytes used in this study are depicted in Figs. 2 and 3, respectively. The effect of steric factors on enantiomeric separation was examined using BNP, BOH, BNA, TFAE, and AG. The binaphthyl derivatives, BOH, BNA, and BNP, possess chiral planes rather than chiral centers unlike TFAE and AG which possess stereogenic centers. Chiral planes are a result of restricted rotation about a central bond resulting in $C_2$ symmetry [38].

### *3.3. Hydrogen bonding and rigidity*

The effects of hydrogen bonding capabilities and rigidity of the chiral selector were investigated through a comparison of poly(L-SUNV) with poly(L-SUP). The C2 of the amino acids of poly(L-SUNV) and poly(L-SUP) both contain three carbon atoms. However, the C2 of the amino acid on poly(L-SUP) is connected to the nitrogen atom (Fig. 2) resulting in a cyclic amino acid which does not contain an amide hydrogen. Therefore, poly(L-SUP) lacks a hydrogen bonding site which can participate in enantiomeric interactions with the analyte. The C2 of the amino acid on poly(L-SUNV) is a straight three-carbon atom chain (Fig. 2). The differences in the structures of poly(L-SUP) and poly(L-SUNV) result in significantly different enantiomeric resolving capabilities. Compared to poly(L-SUP), poly(L-SUNV) produced higher resolution values for four of the five compounds tested. As indicated in Table 1, the resolution of BOH was 1.57 for poly(L-SUNV) compared to 0.82 for poly(L-SUP). Table 1 also illustrates that poly(L-SUNV) was able to partially resolve BNA, AG, and TFAE with resolution values of 0.93, 0.89, 0.66, respectively, compared to poly(L-SUP) which produced no enantiomeric resolution. For all of the compounds studied poly(L-SUP) had a larger capacity factor ($k$) value than poly(L-SUNV). The differences in enantiomeric selectivity between poly(L-SUNV) and poly(L-SUP) are attributed to the lack of a hydrogen bonding site on the amide

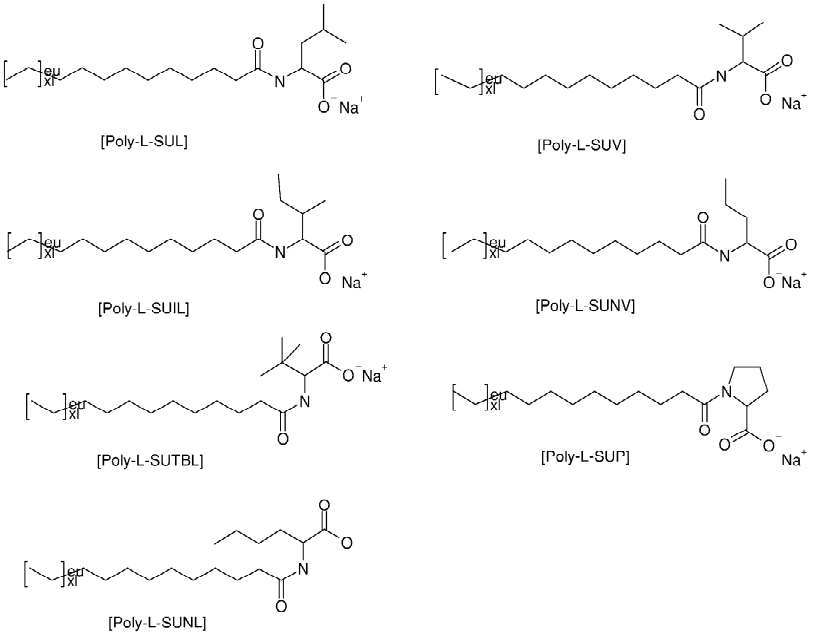


Fig. 2. Structures of surfactant molecules.

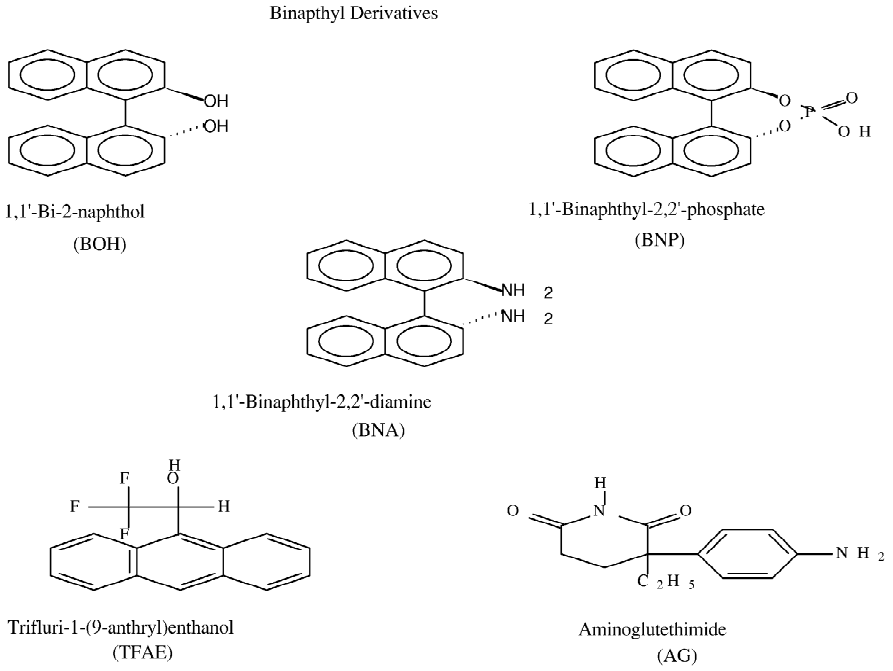


Fig. 3. Structures of analytes.

nitrogen for poly(L-SUP). This seems to be a valid explanation since all of the other factors, hydrophobicity, electrostatic interactions, π-bonding capabilities, between poly(L-SUNV) and poly(L-SUP) appear to be equal. However, this explanation is not valid for explaining the results obtained with BNP.

Table 1
Table of resolution, *k* values and *α* values for the binaphthyls, AG and TFAE

| | BOH | | BNA | | BNP | | AG | | TFAE | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *Rs* | *k* | *Rs* | *k* | *Rs* | *k* | *Rs* | *k* | *Rs* | *k* |
| | *α* | | *α* | | *α* | | *α* | | *α* | |
| Poly(L-SUL) | 2.22 | 0.96 | 1.10 | 0.91 | 0.00 | 0.80 | 1.10 | 0.47 | 0.63 | 1.99 |
| | 1.08 | | 1.09 | | 1.00 | | 1.07 | | 1.53 | |
| Poly(L-SUIL) | 1.36 | 0.88 | 1.35 | 0.84 | 0.59 | 0.82 | 1.08 | 0.58 | 1.19 | 2.53 |
| | 1.06 | | 1.09 | | 1.02 | | 1.08 | | 1.45 | |
| Poly(L-SUNL) | 0.92 | 0.85 | 0.64 | 0.83 | 0.00 | 0.83 | 0.00 | 0.48 | 0.00 | 2.44 |
| | 1.04 | | 1.06 | | 1.00 | | 1.00 | | 1.00 | |
| Poly(L-SUTBL) | 0.00 | 0.95 | 0.85 | 0.86 | 0.00 | 0.83 | 0.00 | 0.50 | 0.00 | 2.16 |
| | 1.00 | | 1.07 | | 1.00 | | 1.00 | | 1.00 | |
| Poly(L-SUV) | 1.53 | 0.83 | 0.68 | 0.84 | 0.00 | 0.82 | 1.09 | 0.53 | 0.77 | 2.17 |
| | 1.07 | | 1.07 | | 1.00 | | 1.06 | | 1.50 | |
| Poly(L-SUNV) | 1.57 | 0.84 | 0.93 | 0.83 | 0.00 | 0.92 | 0.89 | 0.46 | 0.66 | 2.25 |
| | 1.07 | | 1.07 | | 1.00 | | 1.07 | | 1.47 | |
| Poly(L-SUP) | 0.82 | 1.04 | 0.00 | 1.02 | 0.99 | 1.10 | 0.00 | 0.49 | 0.00 | 2.63 |
| | 1.03 | | 1.00 | | 1.03 | | 1.00 | | 1.00 | |

Conditions for binaphthyls: +25 kV, 30 m*M* borate, pH 10, 2 s pressure injection of 0.05 mg/ml sample. Conditions for AG and TFAE: 21 m*M* surfactant, +25 kV, 200 m*M* borate/50 m*M* dibasic phosphate, pH 7.1, 2 s pressure injection of 0.05 mg/ml sample.

Poly(L-SUP) was the only selector besides poly(L-SUIL) able to resolve BNP. BNP was separated with a resolution of 0.99 using poly(L-SUP) compared to no resolution for poly(L-SUNV) (Table 1). The difference in resolution between the two selectors for BNP is believed to be due to the rigidity of the selector and analyte. BNP is a rigid compound due to the phosphorous atom linking the two naphthyl rings. The head group of poly(L-SUP) is also rigid due to the cyclic nature of the amino acid. In the absence of hydrogen bonding, structural rigidity of the complex is believed to impart the necessary enantiomeric selectivity. In contrast, the C2 of the amino acid on poly(L-SUNV) does not allow for a rigid complex to form with BNP thus, the inability of poly(L-SUNV) to resolve BNP. The ability of poly(L-SUIL) to partially resolve BNP will be discussed later.

### *3.4. Steric factors near the chiral center*

Examining the role of steric hindrance near the chiral center with regard to enantiomeric separations was accomplished by comparing poly(L-SUTBL), poly(L-SUL), and poly(L-SUNL). Poly(L-SUTBL), poly(L-SUL), and poly(L-SUNL) were chosen because of the decrease in steric factors near the chiral center moving from poly(L-SUTBL) to poly(L-SUNL). Table 1 indicates these polymeric surfactants have similar *k* values for all of the compounds compared. Differences in enantiomeric resolution can be attributed to steric differences between these surfactants. As shown in Table 1, poly(L-SUL), poly(L-SUNL), and poly(L-SUTBL) are able to partially separate BNA with *Rs* values of 1.10, 0.64, 0.85, respectively. BNA was the only compound that poly(L-SUTBL) was able to separate (Table 1). The inability of poly(L-SUTBL) to separate the enantiomers of any of the other analytes is attributed to the bulkiness of the tert.-butyl group connected to the stereogenic center. It is believed that the tert.-butyl group prevents interactions from occurring between the amide hydrogen on poly(L-SUTBL) and the analyte. The importance of interactions with the amide group for enantiomeric separation was clearly demonstrated with poly(L-SUP). Poly(L-SUL) produced the highest resolution for four out of the five compounds tested compared to poly(L-SUNL) and poly(L-SUTBL). As seen in Table 1, the enantiomeric resolutions for BOH, AG, TFAE obtained with poly(L-SUL) are 2.22, 1.10, and 0.63, respectively. The increase in resolution for poly(L-SUL) is thought to occur because the C2 of the amino acids on poly(L-SUL) is not bulky enough, like poly(L-SUTBL), to prevent enantiomeric interactions with the analyte. Discussion of the poor resolution produced by poly(L-SUNL) is addressed in the following section.

### *3.5. Effect of chain length*

Determining the effect of chain length on enantiomeric recognition was accomplished by comparing poly(L-SUL) to poly(L-SUV) and poly(L-SUNV) to poly(L-SUNL). As observed in Fig. 3, these surfactants have similar hydrophobicities which allows for direct comparison of the C2 of the amino acids length on enantiomeric resolution. The only significant difference between poly(L-SUL) and poly(L-SUV) is in the resolution of BOH. Table 1 shows that poly(L-SUL) separated BOH with an enantiomeric resolution value of 2.22 compared to poly(L-SUV) which separated BOH with an enantiomeric resolution value of 1.53. Resolution of BNA, TFAE, and AG was similar for both poly(L-SUL) and poly(L-SUV). These results indicate that a chain length of one or two carbons does not significantly effect enantiomeric resolution. Furthermore, Table 1 shows there is no significant difference in the enantiomeric resolution of BNA, TFAE, and AG for poly(L-SUL), poly(L-SUV), or poly(L-SUNV). However, a significant decrease in enantiomeric resolution is observed for poly(L-SUNL).

For all of the compounds tested poly(L-SUNV) was a better pseudo-stationary phase than poly(L-SUNL). Table 1 demonstrates that poly(L-SUNV) is able to separate BOH and BNA with enantiomeric resolution of 1.57 and 0.93, respectively, while poly(L-SUNL) separated BOH and BNA with an enantiomeric resolution of 0.92 and 0.64, respectively. Poly(L-SUNV) was able to partially resolve TFAE and AG with a value of 0.66 and 0.89 while poly(L-SUNL) was unable to separate these compounds. The decrease in enantiomeric resolution is attributed to an extra carbon on the poly(L-SUNL) which may not allow for enantiomeric overlap or which may block the analyte's access to the amide

hydrogen. These studies seem to indicate that a four-carbon straight chain reduces enantiomeric separation.

### 3.6. Effect of two chiral centers

To assess the effect of two chiral centers located on poly(L-SUIL) head group, poly(L-SUIL) was compared to the other polymeric surfactants except poly(L-SUP). By comparing poly(L-SUIL) to the other polymers all possible differences except the addition of the extra chiral center can be investigated. Table 1 indicates that poly(L-SUIL) was able to separate four out of the five compounds analyzed with higher or equal resolution values compared to the other polymers. Poly(L-SUIL) separated BNA, BNP, TFAE and AG with enantiomeric resolution values of 1.35, 0.59, 1.19 and 1.09, respectively. Only poly(L-SUL) ($Rs = 2.22$) was able to separate BOH with a higher resolution than poly(L-SUIL) ($Rs = 1.36$). The higher enantiomeric resolution values obtained with poly(L-SUIL) for the majority of the compounds is believed to occur because of the extra chiral center located on the C2 of the amino acids. The additional chiral center is less sterically restricted compared to the chiral center located on the amino acid backbone. The flexibility of the chiral center increases enantiomeric resolution by providing a site of interaction which is easily accessible to the analyte.

## 4. Conclusions

The isolation of steric effects from other considerations has led to the observance of notable trends. The data clearly show that the shape of the selector near the stereogenic center has an effect on the separation of enantiomers. In the comparison of poly(L-SUV), poly(L-SUL) and poly(L-SUTBL), poly(L-SUTBL) was found to be the worst selector because access to the chiral center was sterically hindered by the tert.-butyl group. Poly(L-SUP) showed that certain analytes are separated better by rigid selectors, however; for the most the amide hydrogen on the amino acid head group is necessary for enantiomeric resolution. Poly(L-SUNV) and poly(L-SUNL) indicated that the length of the side chain can effect the enantiomeric resolution. Poly(L-SUNL) demonstrates that if the carbon chain is longer than four carbons a decrease in enantiomeric resolution results for the compounds tested. Poly(L-SUIL) showed that addition of an extra chiral center can increase the enantiomeric selectivity of the polymer. This presumably occurs because the chiral center on the polymer is not as sterically hindered and the chiral center is closer which provides for better interaction with the analyte.

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