

CHAPTER III

EXPERIMENTAL

In the present work of mixed solvent of crystallization step of C₄-LLDPE, C₆-LLDPE and C₈-LLDPE with preparative TREF technique, the experiment was divided into four steps.

1. Operational testing of preparative TREF apparatus.
2. Study of branching content by means of ¹³C-NMR spectroscopy.
3. Crystallization of LLDPE by using xylene.
4. Crystallization of LLDPE by using mixed xylene solvents.

The detail of the experiments was explained in the following.

3.1 Reagents and solvents

The reagents and solvents in this experiment were analytical grade.

Table 3.1 Chemical reagents and suppliers

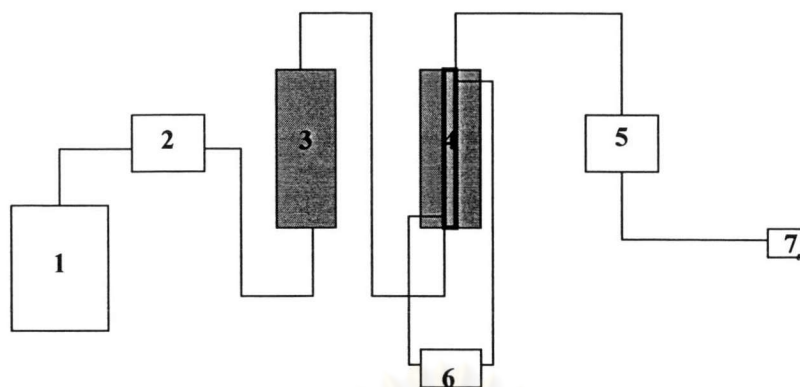
Reagents and Solvents	Supplier
xylene	Scharlau Chemie S.A., Spain
methanol	Merck, Germany
acetone	Merck, Germany
Irganox 1010	Lab Scans Co., Ltd., Ireland
silicone oil	Down Corning., USA
ethylene glycol	Lab Scans Co., Ltd., Ireland
glycerol	Merck, Germany

3.1.1 Linear Low Density Polyethylene (LLDPE)

There are three LLDPE samples i.e. ethylene/1-butene copolymers (C₄-LLDPE), ethylene/1-hexene copolymers (C₆-LLDPE), and ethylene/1-octene copolymers (C₈-LLDPE). All samples were donated by Thai Polyethylene Co., Ltd. (TPE), Thailand.

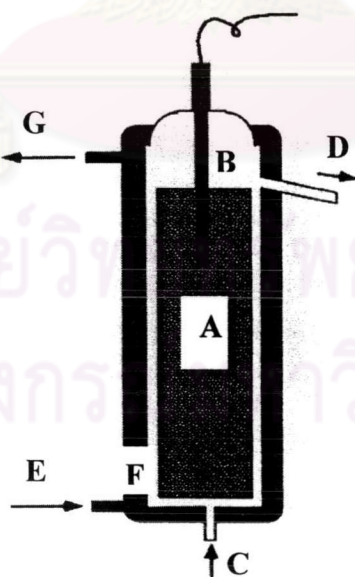
3.2 Preparative TREF apparatus

The instrumental setup consists of a high pressure liquid chromatography (HPLC) pump (Series III pump), constant temperature circulators (JULABO-MWF33), a stainless steel column (1.0 cm inner diameter, 49.0 cm length), solvent reservoir, and fraction collector. The configuration of TREF apparatus was shown as in scheme 3.1. The TREF columns utilized in the system were stainless steel columns loaded with 15 g glass beads. It is schematically described in Scheme 3.2. It consists of a one-tube glass and stainless steel column packed with glass beads (part A). The glass beads have a 2 mm diameter prior to loading into the column. The temperature of the column is controlled using a temperature controller consisting of a silicon oil bath, circulating the oil through the outer tube of the column (parts E, F, and G), equipped with a thermostat. A thermal probe inserted in the top of the column allows us to measure the temperature inside the column (part B), as shown in scheme 3.2. For the elution of the different fractions, the column is connected to a system through which the solvent was pumped at a flow rate of 1.5 mL/min (parts C and D).



1 = Solvent reservoir	3 = Pre-column	5 = RI Detector	7 = Fraction collector
2 = Pump	4 = column	6 = Circulator bath	

Scheme 3.1 Schematic illustration of preparative TREF.



Scheme 3.2 Schematic view of the preparative TREF column.

3.3 Preparative TREF using single solvent

3.3.1 C₄-LLDPE

A 0.5 g sample of C₄-LLDPE was completely dissolved in 30 ml of hot xylene with 0.1 g of Irganox 1010 as an antioxidant at 120°C, and hold for 30 min. Then the polymer solution was transferred to the TREF column loaded with 15 g of glass beads as an inert support. The TREF column was capped and cooled down from 120°C to 20°C with a cooling rate of 1°C/h. The cooling rate were also varied to 3°C/h, 5°C/h, 7°C/h, 8°C/h, and 10°C/h. When the temperature was stable at 20°C for 30 min, the temperature was raised up from 20°C to 120°C with cooling rate of 10°C/h stepwise. Then the fractionated polymer was collected at 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, and 120°C, respectively. The collected polymer was precipitated with pure methanol, dried and weighed. The experiment of LLDPE samples was performed three times for each one. Finally the weight percent was calculated as equation below. The cumulative fraction was investigated branching content and melting behavior by NMR and DSC, respectively.

$$\text{Weight percent (wt\%)} = \frac{\text{weight of fractionated polymer} \times 100}{\text{weight of polymer sample}} \quad \dots\dots(1)$$

3.3.2 C₆-LLDPE

A 0.5 g sample of C₆-LLDPE was completely dissolved in 30 ml of hot xylene with 0.1 g of Irganox 1010 as an antioxidant at 120°C, and hold for 30 min. Then the polymer solution was transferred to the TREF column loaded with 15 g of glass beads as an inert support. The TREF column was capped and cooled down from 120°C to 20°C with a cooling rate of 1°C/h. The cooling rates were also varied to 2°C/h, 3°C/h,

and 5°C/h. When the temperature was stable at 20°C for 30 min, the temperature was raised up from 20°C to 120°C with rate 10°C/h stepwise. Then the fractionated polymer was collected at 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, and 120°C, respectively. The collected polymer was precipitated with pure methanol, dried and weighed. The experiment of LLDPE samples was performed three times for each one. Finally the weight percent was calculated as equation (1). The cumulative fraction was investigated branching content and melting behavior by NMR and DSC, respectively.

3.3.3 C₈-LLDPE

The procedure condition of C₈-LLDPE was the same as the manner of preparative TREF of C₆-LLDPE.

3.4 Preparative TREF using mixed solvent

3.4.1 Ethylene glycol in xylene

For determining the proper percentage of ethylene glycol in xylene, the non-solvent like ethylene glycol (EG) concentration was varied from 0.1% to 1.0% was impured into xylene as a good solvent for crystallizing three kinds of LLDPE samples such as C₄-LLDPE, C₆-LLDPE, and C₈-LLDPE, respectively. The procedure condition was the same as the manner of preparative TREF in single solvent system. Except, measured DSC and GPC. The major fractions of C₆-LLDPE, and C₈-LLDPE were observed.

3.4.2 Glycerol in xylene

For determining the proper percentage of glycerol in xylene, the non-solvent like glycerol concentration was varied from 0.1% to 1.0% was impured into xylene as a good solvent for crystallizing three kinds of LLDPE samples such as C₄-LLDPE, C₆-LLDPE, and C₈-LLDPE, respectively. The procedure condition was the same as the manner of preparative TREF in single solvent system. Except, measured DSC and GPC. The major fractions of C₆-LLDPE, and C₈-LLDPE were observed.

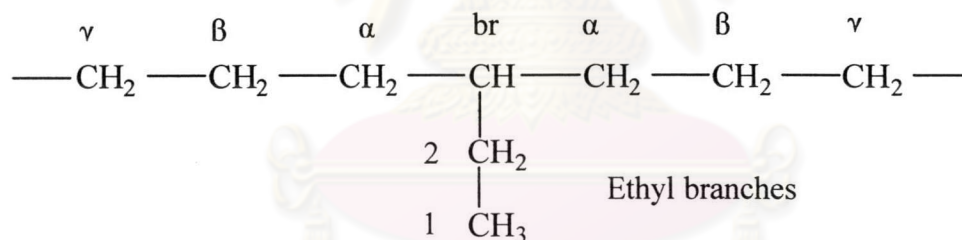
3.5 Branching content determination by ¹³C-NMR spectroscopy [49-54]

¹³C-NMR spectra were obtained with a Jeol JNM-A 500 MHz FT-NMR spectrometer. The polymer samples were dissolved in benzene-d and ODCB at 130°C. ¹³C-NMR spectra were used for the determination of branching content. A pulse program with flip angle of 90°C was used, matching with 2 s acquisition time and 12 s relaxation delay in the sweep width of 175 ppm. To eliminate nuclear overhauser enhancement effect (NOE), an inverse-gate decoupling pulse program was selected. The chemical shift assignments of polymer chains followed ASTM D 5017-91 method which was shown in Appendix A-1. The center peak of polymer samples were used as the internal reference (at 30 ppm., isolated methylene carbons). The fractionated polymer was weighed around 0.12 g and dissolved into a 10 mm NMR tube by 0.6 ml of ODCB and 0.1 ml deuterated benzene as an internal signal lock. Then the tube was capped. The sample was homogenized in an oven at 120°C for 3 to 4 h, then at 145-150°C for 2 h, and kept in an horizontal position during the heating step and transferred to the NMR spectrometer and equilibrated 10 to 15 min at 130°C. The spectrum was recorded. The integration limit of each LLDPE was shown as Appendix A.1. The calculated branching content of each LLDPE was shown in the bottom equations following.

3.5.1 C₄-LLDPE

¹³C-NMR spectrum for the ethylene/1-butene copolymers is divided into regions as dictated by resolution and certainty in assignments. The methane and branch methylene resonances also overlap badly with nearby polymer backbone methylene resonances. The representative ¹³C-NMR spectrum of C₄-LLDPE was given in Figure 3.1 with assignments. Where A, A', B, C, D, E and F are the area under peaks which were assigned in Appendix A (see Table A-1 to Table A-3).

The integration limits given below not only take into account for the isolated branches, but also branches which are separated by one ethylene unit and branches next to each other. The terminology of C₄-LLDPE for branching was shown as below.



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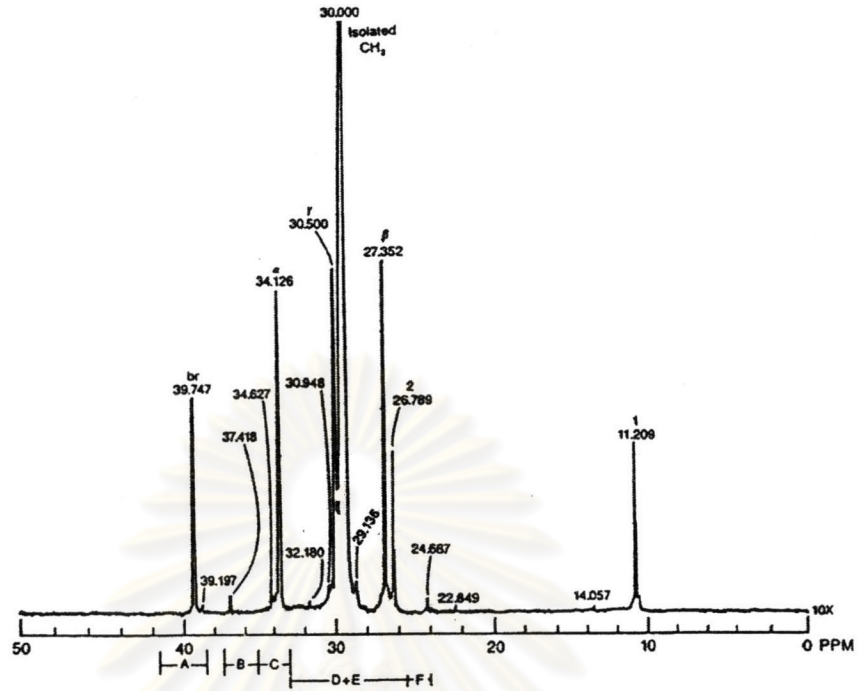


Figure 3.1 ^{13}C -NMR spectrum of ethylene/1-butene copolymers.

From the recorded spectrum, mol% co-monomer of C_4 -LLDPE can be calculated by

$$\text{Mole\% 1-butene} = 100\% \times B' / (B' + E')$$

When

$$B_1 = \alpha - \text{carbons: } (2A + B)/2$$

$$B_2 = \text{CH carbons: } (A' + 2B + 2C)/4$$

$$B' = \text{average moles 1-butene: } (B_1 + B_2)/2$$

$$E' = \text{moles ethene: } (2D + 2E + 2F - A' - B)/4$$

Therefore, the branching content of C_4 -LLDPE can be calculated by

$$\text{Branching content} = \frac{1000(\text{mole\%1-butene})}{2(\text{mole\%ethene}) + 4(\text{mole\%1-butene})}$$

3.5.2 C₆-LLDPE

The representative ¹³C-NMR spectrum of C₆-LLDPE was given in Figure 3.2 with assignments. Where A, B, C, D, E, F, G and H are the area under peaks which were assigned in Appendix A (see Table A-1, Table A-2, and Table A-4). The integration limits given below not only take into account for the isolated branches, but also branches which are separated by one ethylene unit and branches next to each other. The terminology of C₆-LLDPE for branching was shown as below.

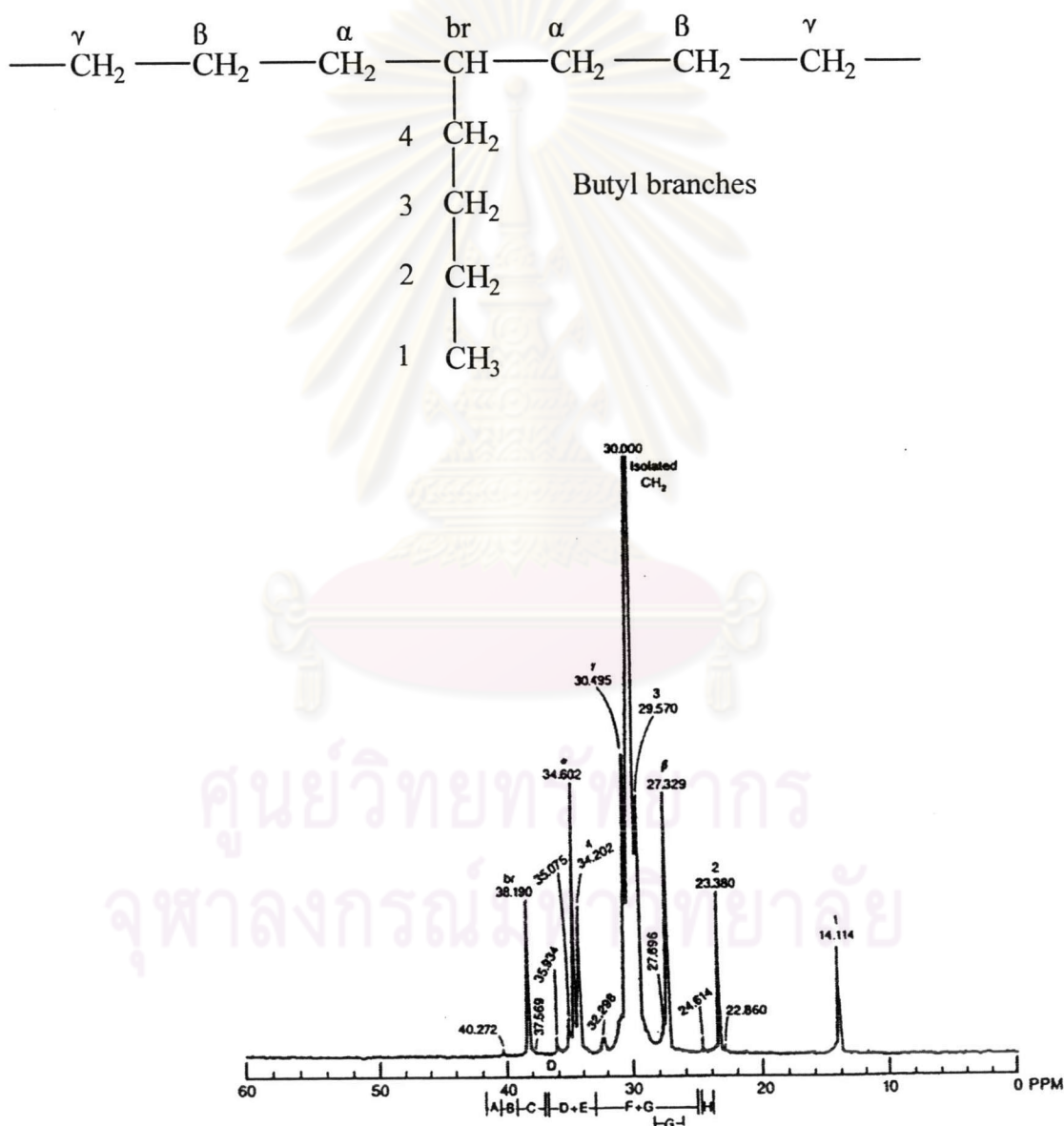


Figure 3.2 ¹³C-NMR spectrum of ethylene/1-hexene copolymers.

From the recorded spectrum, mol% co-monomer of C₆-LLDPE can be calculated by

$$\text{Mole\% 1-hexene} = 100\% \times H' / (H' + E')$$

When

$$H_1 = \alpha - \text{carbons: } [1.5A + 2B + (D + E) - D]/3$$

$$H_2 = \text{CH carbons: } (A + 2C + 2D)/2$$

$$H' = \text{average moles 1-hexene: } (H_1 + H_2)/2$$

$$E' = \text{moles ethene: } [(F + G) - 3A - 3B - G - H]/2 + H'$$

Therefore, the branching content of C₆-LLDPE can be calculated by

$$\text{Branching content} = \frac{1000(\text{mole\%1-hexene})}{2(\text{mole\%ethene}) + 6(\text{mole\%1-hexene})}$$

3.5.3 C₈-LLDPE

The representative ¹³C-NMR spectrum of C₈-LLDPE was given in Figure 3.3 with assignments. Where A, B, C, D, E, F, G, H, I and P are the area under peaks which were assigned in Appendix A (see Table A-1, Table A-2, and Table A-5). The integration limits given below not only take into account for the isolated branches, but also branches which are separated by one ethylene unit and branches next to each other. The terminology of C₈-LLDPE for branching was shown as below.

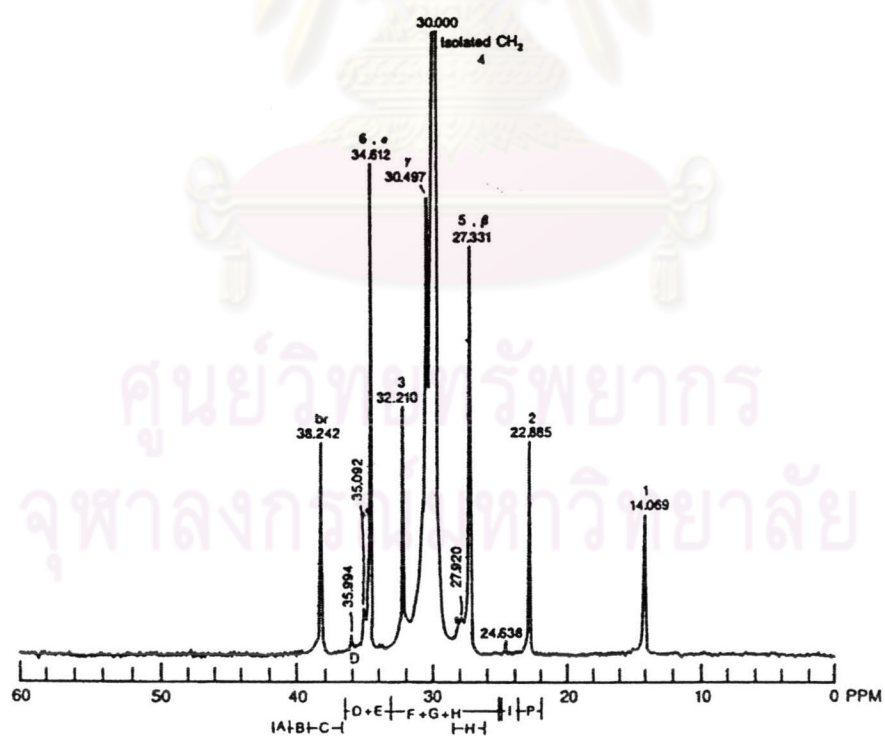
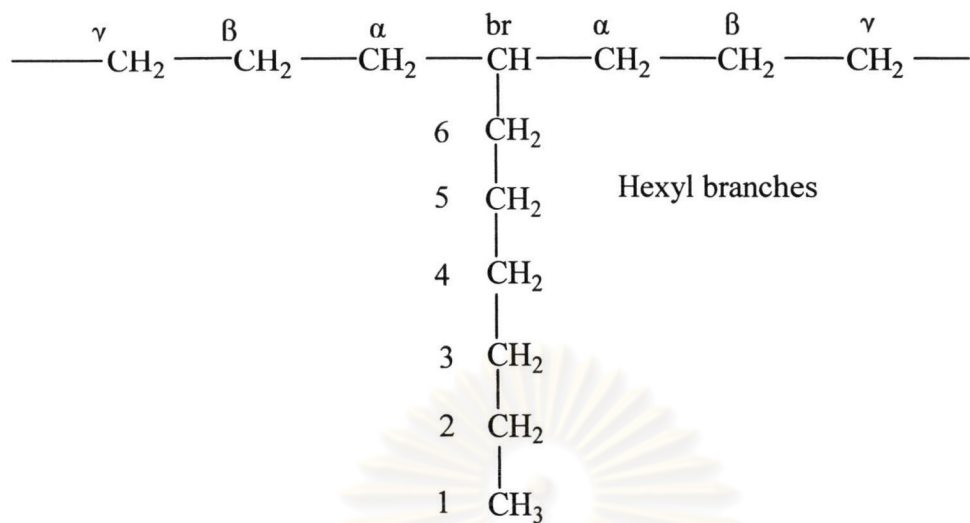


Figure 3.3 ^{13}C -NMR spectrum of ethylene/1-octene copolymers.

From the recorded spectrum, mol% co-monomer of C₈-LLDPE can be calculated by

$$\text{Mole\% 1-octene} = 100\% \times O' / (O' + E')$$

When

$$O_1 = \alpha - \text{carbons: } (A + 2C + 2D)/2$$

$$O_2 = \text{CH carbons: } [1.5A + 2B + (D + E) - D]/3$$

$$O' = \text{average moles 1-octene: } (O_1 + O_2)/2$$

$$E' = \text{moles ethene: } [(F + G + H) - (3A + 3B + H + P + D)]/2 + O'$$

Therefore, the branching content of C₈-LLDPE can be calculated by

$$\text{Branching content} = \frac{1000(\text{mole\%1-octene})}{2(\text{mole\%ethene}) + 8(\text{mole\%1-octene})}$$

The example calculation for branching content determination by ¹³C-NMR spectroscopy was shown as Appendix A (see A.2). The integral values of each area of LLDPEs was shown as Appendix A (see A.3).

3.6 Measurements of melting temperature by DSC [55]

A Mettler Toledo Star System differential scanning calorimeter was used for the thermal analyses. Samples, weighing about 2-5 mg, were sealed in crimped aluminum pans. The peak area and temperature calibration were performed using pure indium. The melting behavior of each LLDPE whole polymer and its fraction at cooling rate 1°C/h of single solvent system was studied. The sample were heated to 170°C and maintained for 15 min, cool at either 1 or 20°C/min to 30°C, and reheated at 20°C/min to 170°C. Both heating and cooling thermograms were collected. The DSC thermogram of each fractionated polymer and whole polymer were showed in Appendix B.

3.7 Characterization of molecular weight distribution by GPC [55]

Molecular weight and molecular weight distribution of whole polymer samples (see in Appendix C) were determined using a Waters 150 C gel permeation chromatography. Two hundred microliters of a 0.5% solution of polyethylene in TCB was injected at a flow rate of 1.0 mL/min onto a column set consisting of three Styragel packed (Water Inc.) 3/8 X 18 in. columns (one each of 10^4 , 10^5 , and 10^6 Å). The columns were calibrated using narrow polystyrene standards and narrow fractions of linear, unbranched polyethylene. The polystyrene standards were assigned polyethylene molecular weights based on polystyrene versus polyethylene standards curve. Polystyrenes were used because of their commercial availability.