Chapter 4. Materials Characterization

It was mentioned in the previous chapter that some of the statistical properties of the comonomer sequence distribution in ethylene/α-olefin copolymers can be determined by means of ^{13}C NMR spectroscopy. The results of those experiments are discussed in this chapter. In addition, the results of the macroscopic density measurements using the density gradient column are also reported. The densities were measured as a function of crystallization time, and are also compared to those obtained from the literature. Mr. Ley Richardson is acknowledged for the density gradient column measurements.

4.1 Characterization Using ^{13}C NMR

4.1.1 Peak Assignments

Before proceeding with the interpretation of the NMR spectra collected for the copolymers, it is useful to review briefly the signals associated with the different types of carbon atoms in the copolymer chain. The discussion presented below is limited to the branch types present in the copolymers examined. More comprehensive surveys are available in the literature.[1,2,3,4,5,6,7]

In order to derive meaningful results from the NMR study, it is essential to recognize that the presence of a comonomer, say 1-butene (C_4) results in the incorporation of two of the carbon atoms into the polymer backbone, resulting in an ethyl (C_2) branch. Accordingly, the 1-pentene (C_5) and 1-hexene (C_6) comonomers yield propyl (C_3) and butyl (C_4) side groups, respectively. A combination of numerals and Greek letters is usually utilized in the numbering system employed for the identification of the various carbon atoms, as shown schematically in Figure 1.

Then, we proceed to consider the general characteristics of a typical ^{13}C NMR spectrum of an ethylene/α-olefin copolymer (also similar to the spectrum of low density polyethylene). The spectra of all the ethylene copolymers are dominated by a strong central peak at ~ 29.99 ppm, arising from the resonance of the γ and δ CH_2 moieties. It has been reported in the literature[1] that the presence of an ethyl branch invariably gives rise to a resonance at ~ 10.94 ppm in the ^{13}C spectrum of the sample. This signal is assigned to the methyl carbon (C1 in the figure above) of the branch. A weaker resonance at ~ 39.1 ppm due to the methine carbon (the carbon labeled with Br) may also be discerned in some samples. Although the intensity of this peak in the copolymers studied (in the present study) was fairly moderate, this peak may be extremely weak or ill defined for some samples.

The occurrence of branches in the 1, 3- position as shown in Figure 2 can also be determined from the spectra collected. The methine carbon atoms in this arrangement are expected to resonate upfield compared to those associated with the isolated ethyl branches indicated in Figure 1. Therefore, a signal at ~ 37.8 ppm corresponding to these methine carbons and a weaker one at ~ 38.5 ppm corresponding to the A methylene carbon in the backbone may be used to identify uniquely the 1, 3-ethyl branch sequence in the copolymer. For the samples studied here, the resonance at 37.8 ppm can only be observed in the spectra of the more highly branched copolymers (≥ 9 mole % branches). Furthermore, the intensity of the peak, even in this range of branch contents, was found to decrease significantly for lower comonomer contents. This result is contrary to those arrived at by Dechter and Mandelkern[3] that "there does not appear to be any correlation between the total ethyl branching level and the occurrence of 1,3-diethyl branching". This discrepancy is easily understood on the basis of the higher fields and sensitivity allowed by the modern NMR equipment, in contrast to those used in the early 80's by Dechter and Mandelkern.

The occurrence of propyl branches were characterized by the following unique resonances:

1. ~ 20.85 ppm due to the methylene carbon (C2) of the propyl branch, and
2. ~ 14.6 ppm due to the methyl carbon (C1) of the branch.

Signals arising at the chemical shift of the C3 methylene carbon of the propyl branch appeared at ~ 37 ppm. However, the signal due to the methine carbon of the branch (Br) also occured in the same region, significantly overlapping with the above signal.

Therefore, it was not possible to employ this resonance as a unique means of identifying the propyl branch.

The presence of butyl branches in the ethylene/1-hexene copolymers was estimated from the intensities of the signals at,

1. 14.2 ppm due to the methyl carbon (C1) of the butyl branch, and
2. 23.34 ppm due to the C2 methylene carbon of the branch.

Other resonances due to the methine carbon (Br) at ~38 ppm and the C4 methylene carbon of the branch at ~ 34 ppm also appeared in the spectra of these samples. However, as pointed out earlier for the case of propyl branches, these signals overlapped considerably with those arising from other carbons. As a result, they were not used in the determination of butyl branch concentration of the copolymers. A summary of the peak assignments discussed above is provided in Table 1. A more comprehensive summary of the chemical shifts associated with the various carbon atoms in these copolymers is available in Reference 1.

Any resonance arising from the presence of 1,2-diethyl branches is evidence of head-to-head addition during copolymerization. The arrangement of carbon atoms in this case is schematically shown in Figure 3.

Cudby and Bunn[8] have investigated the NMR spectra of an ethylene/1-butene copolymer with ~ 30 mole % comonomer. It is known from their results as well as from other similar studies[3,9] that the chemical shifts due to the presence of branches on adjacent carbon atoms in such copolymers may be used to pinpoint the occurrence of the 1,2- branches. Some of these include:

1. A resonance at ~ 9.92 ppm assigned to the methyl carbons (C1) of the 1,2-diethyl branches.
2. A weak signal at ~ 24.57 ppm assigned to the methylene carbon atoms (C2) of the branches.
3. A clear and strong signal at ~ 41.3 ppm due to the methine carbon atoms (Br) of the adjacent branches, and
4. A signal at ~ 31.73 ppm attributed to the chemical shift of the α-methylene carbon atom of the backbone in the structure depicted in Figure 3.

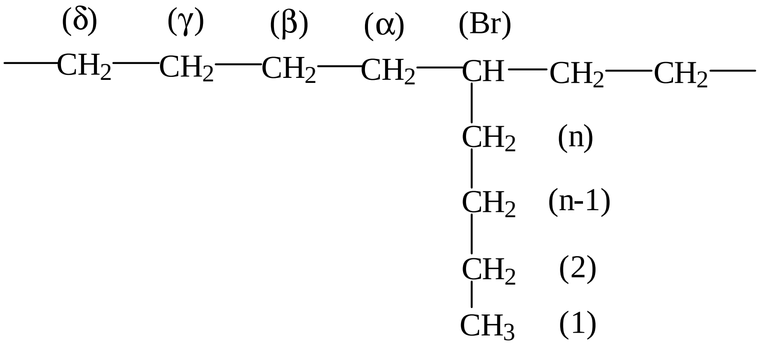

Figure 1 Numbering scheme for the identification of carbon atoms in the ^{13}C NMR spectra of an ethylene/α-olefin copolymer (Adopted from Ref. 1).

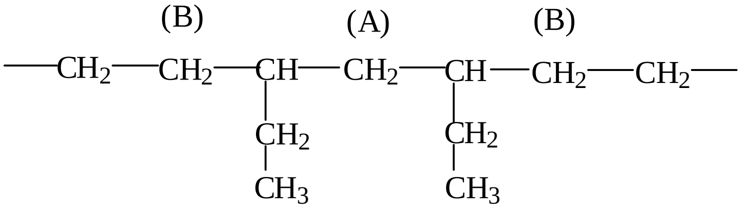

Figure 2 Ethyl branches in the 1,3-position (Adopted from Ref. 1).

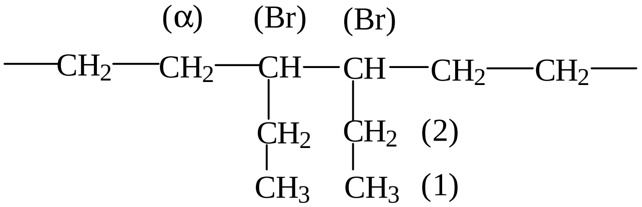

Figure 3 Ethyl branches in the 1,2-position, indicating head-to-head addition

Table 1 Peak assignments for the determination of branch content from the NMR spectra of ethylene/α-olefin copolymers

Chemical Shift (ppm)	Assignment
Ethyl Branch	
~ 29.99	γ and δ methylene carbon of backbone
~ 39.1	Methine carbon (Br)
~ 10.94	Methyl carbon (C1) of ethyl branch
1,3-Position of Ethyl Branch (Figure 2)	
~ 37.8	Methine carbon
~38.5	"A" methylene carbon
Propyl Branch	
~ 14.6	Methyl carbon (C1) of propyl branch
~ 20.85	Methylene carbon (C2) of propyl branch
~37	Methylene (C3) of propyl branch
Butyl Branch	
~38	Methine carbon (Br)
~14.2	Methyl (C1) of butyl branch
~23.34	Methylene (C2) of butyl branch
~34	Methylene (C4) of butyl branch

4.1.2 Branch Content Determination from Assigned Resonances

The concentration of branches (in mole percent) in the ethylene/1-butene copolymers was estimated from the intensities of the signals corresponding to the methyl and methylene carbons of the branches, as expressed in the following equation.

$$(1) \qquad Mole\,\%\,branches = \frac{I_{10.94} + I_{39.86}}{\left[I_{total} - (I_{10.94} + I_{39.86})\right]}$$

where I_{total} = the sum of the integrated intensities of all the signals appearing in the sample spectrum. The positions and intensities of the signals used in the calculations for the ethylene/1-pentene and ethylene/1-hexene copolymers are listed in Table 2. The number of branches per 1000 carbons, n_b, is determined in each case using the expression,

$$(2) \qquad n_b = \frac{Mole\,\%\,branches}{100} \times 500$$

The values of n_b obtained for the copolymers are also listed in Table 2, along with the values provided by the suppliers. A close agreement is observed.

Table 2 The integrated intensities of the significant bands in the ^{13}C NMR spectra of the ethylene copolymers. The mole percent branches and the number of branches per 1000 carbon atoms are also included.

Sample	10.94 ppm	39.86 ppm	Total	Mole % branches	n_b	Mole % branches (Dow)
EB-928	-	-	-	-	-	1.45
EB-912	3.50	3.96	182.89	4.25 ± 0.70	21	4.61
EB-894	6.99	7.63	186.88	8.49 ± 0.73	45	8.97
EB-883	12.24	9.04	187.57	12.79 ± 0.778	64	12.6
EB-879	12.93	10.61	194.78	13.75 ± 0.748	69	13.7
EB-874	19.21	16.87	263.20	15.89 ± 0.568	80	15.8

Sample	14.60 ppm	20.85 ppm	Total	Mole % branches	n_b	Mole % branches (Dow)
EP-910	7.31	6.81	317.56	4.65 ± 0.41	23	4.44
EP-870	30.10	29.26	456.06	14.96 ± 0.329	75	14.31

Sample	14.20 ppm	23.34 ppm	Total	Mole % branches	n_b	Mole % branches (Dow)
EH-910	2.95	1.79	155.00	3.16 ± 0.81	16	3.60
EH-886	9.10	8.98	193.38	10.31 ± 0.726	52	10.7
EH-869	30.43	28.83	463.06	14.68 ± 0.315	73	14.2

4.1.3 Microstructure Analysis

A single chain in a copolymer comprised of A and B units may be visualized as being made up of any one or all of the following types of contiguous repeat units:

4 Diads: (AA), (AB/BA) and (BB)

8 Triads: (AAA), (AAB/BAA), (BAB), (ABA), (ABB/BBA) and (BBB)

12 Tetrads: (AAAA), (BAAA/AAAB), (BAAB), (AABA/ABAA), (AABB/BBAA), (BABA/ABAB), (BBAB/BABB), (ABBA), (BBBA/ABBB) and (BBBB) and pentads and so on.

The concentration of such units can be determined from the NMR spectrum of a given copolymer.[10] In other words, it is possible to determine the total number of ways in which A and B may be combined within a given sequence length, without having to know the length of the longest sequence. In addition, structural information of this type may be obtained from any of the *n*-ad distributions, since the various *n*-ad types mentioned above are related to each other by means of "necessary relationships".[11] A detailed survey of these relationships is available in Randall's review[10] on sequence determination via ^{13}C NMR Spectroscopy. In the present study, microstructural information on the arrangement of the ethylene and comonomer units was obtained from a detailed analysis of the triad sequence distributions. These distributions were determined following the method of Randall.[2,6,10] This method also allows the estimation of comonomer content in the samples. The procedure adopted is described below, followed by the results and calculations.

4.1.3.1 Ethylene/1-Butene Copolymers

The NMR spectra of the ethylene/1-butene copolymers were divided into seven regions according to the chemical shift of the carbon atoms. These regions were defined as follows:

Region A - 37-40 ppm
Region B - 37.2 ppm
Region C - 33.5-35.5 ppm

Region D - 29.5-31.5 ppm
Region E - 26-28 ppm
Region F - 24-25 ppm and
Region G - 10.5-11.5 ppm.

The ethylene/1-butene triad concentrations were obtained from the peak areas for each of the regions listed above, using the following set of equations. The A_i's in these equations are the total area under the peaks in the corresponding regions. The NMR constant, *k*, was eliminated by normalization with respect to the sum of all the triad distributions, thereby yielding the absolute values of the triad fractions. The triad distributions calculated for the ethylene/1-butene copolymers in the present study are listed in Table 3.

(3) $k[EEE] = (1/2)\ A_D - (1/4)\ A_E + (1/4)\ A_G$

(4) $k[BEE / EEB] = A_E - A_G$

(5) $k[BEB] = A_F$

(6) $k[EBE] = A_C - A_A - (1/2)\ A_B$

(7) $k[EBB / BBE] = A_B$

(8) $k[BBB] = 2A_A - 2A_C$

The extent of randomness of copolymer microstructure may be defined by a random parameter[12], χ_R, defined as follows for an ethylene/1-butene copolymer:

(9) $$\chi_R = \frac{[EB]}{[E][B]}$$

where [EB] = 2[EBE] + [EBB/BBE] or 2[BEB] + [EEB/BEE], and [E] and [B] were determined from the triad concentrations using the following relationships:

$$[E] = [EEE] + 1/2\,[BEE/EEB] + 1/2\,[EB/BE]$$

$$[B] = [BBB] + 1/2\,[EBB/BBE] + 1/2\,[EB/BE]$$

The expected values of χ_R corresponding to different types of copolymers such as block, alternating, random etc. are defined in Table 4. The χ_R values calculated for the ethylene/1-butene copolymers are listed in Table 5. It is found that these values for all the samples examined are very close to the value of one expected for a Bernoullian distribution (case of random copolymers). The uncertainties of the χ_R values were estimated by assuming that $\Delta[EB] = \Delta[E] = \Delta[B] = 0.001$.

The concentration of the 1-butene comonomer (in mole percent) was determined from the relative proportions of the [EBE], [EBB/BBE] and [BBB] triads and is also listed in Table 5. These values are comparable to the branch concentrations derived from the specific peak areas, as listed in Table 2. It is gratifying to note that the branch concentrations obtained from the two independent methods are in close agreement with each other as well as with the values provided by the supplier.

Table 3 Triad sequence distributions for the ethylene/1-butene copolymers.

Sample	**[EEE]**	**[BEE]**	**[BEB]**	**[EBE]**	**[EBB]**	**[BBB]**
EB928	0.965	0.025	0.000	0.010	0.000	0.000
EB912	0.891	0.079	0.000	0.030	0.000	0.000
EB894	0.706	0.205	0.000	0.074	0.015	0.000
EB883	0.714	0.155	0.015	0.085	0.031	0.000
EB879	0.687	0.179	0.000	0.096	0.037	0.000
EB874	0.649	0.189	0.009	0.099	0.054	0.000

Table 4 Expected values for the random parameter, χ_R for different types of copolymers (Adopted from Ref. 12).

χ_R	Type of Copolymer
$\chi_R = 0$	Completely Block
$\chi_R < 1$	Less Blocky Character
$\chi_R = 1$	Random Statistics
$\chi_R > 1$	More Alternating Character
$\chi_R = 2$	Completely Alternating

Table 5 Branch concentrations of the ethylene/1-butene copolymers from Randall's method.[10] Their random parameters are also included.

	% Branch Content		Random
sample	**via NMR**	**Dow.**	**Parameter**
EB928	0.982±0.891	1.45	1.01±0.04
EB912	3.03±0.59	4.61	1.03±0.02
EB894	8.94±0.60	8.97	1.01±0.01
EB883	11.6±0.65	12.6	0.982±0.005
EB879	13.4±0.62	13.7	0.993±0.004
EB874	15.3±0.47	15.8	0.971±0.004

4.1.3.2 Ethylene/1-Hexene Copolymers

The ethylene/1-hexene triad sequence distributions were evaluated in a manner similar to that described for the ethylene/1-butene copolymers in the previous section. However, there were minor modifications in the division of the copolymer spectra into the various regions for analysis. The chemical shifts associated with the seven contributing regions are given below.

Region A - 39.5-42 ppm
Region B - 38.1 ppm
Region C - 33-36 ppm
Region D - 28.5-31 ppm
Region E - 26.5-27.5 ppm
Region F - 24-25 ppm
Region G - 23.4 ppm and
Region H - 14.1 ppm.

The distributions of triad sequences were estimated from the areas of the peaks under these regions using the following equations.

(10) $k[\mathrm{EEE}] = (1/2)\ A_D - (1/4)\ A_G - (1/4)\ A_E$

(11) $k[\mathrm{EEH}\ /\ \mathrm{HEE}] = A_E$

(12) $k[\mathrm{HEH}] = A_F$

(13) $k[\mathrm{EHE}] = A_B$

(14) $k[\mathrm{EHH}\ /\ \mathrm{HHE}] = 2A_C - 2A_G - 4A_F - 2A_E - 2A_A$

(15) $k[\mathrm{HHH}] = 2A_A - A_C + A_G + 2A_F + A_E$

The triad sequence distributions for the ethylene/1-hexene copolymers determined from the above equations are listed in Table 6. The branch concentrations and random parameters were estimated in a manner similar to that of the ethylene/1-butene copolymers, and are tabulated in Table 7. Once again, excellent agreement between the two independent determinations of branch contents, as well as with the supplier's values is noted. Furthermore, it is also established that these samples also follow the random copolymerization statistics expected for such metallocene-based single-site catalyzed copolymers.

Table 6 Triad sequence distributions for the ethylene/1-hexene copolymers.

Sample	**[EEE]**	**[HEE]**	**[HEH]**	**[EHE]**	**[EHH]**	**[HHH]**
EH910	0.896	0.066	0.000	0.028	0.010	0.000
EH886	0.733	0.153	0.013	0.062	0.038	0.000
EH869	0.796	0.046	0.020	0.092	0.046	0.000

Table 7 Branch concentrations of the ethylene/1-hexene copolymers from Randall's method.[10] Their random parameters are also included.

	% Branch Content		**Random**
sample	**via NMR**	**Dow.**	**Parameter**
EH910	3.79±0.67	3.6	0.906±0.011
EH886	10.0±0.61	10.7	0.995±0.005
EH869	13.8±0.26	14.2	0.968±0.003

4.2 Density Gradient Column Measurements

It was mentioned in the previous chapter that the macroscopic densities of the ethylene/α-olefin copolymers used in the present study were measured using a density gradient column. The results of those measurements are reported in this section. The densities of pre-pressed samples of the copolymers were measured at 23°C, after storage at this temperature for various times. The values of the densities as well as the uncertainties in the measurements are listed in Table 8.

The bulk densities of the ethylene/1-butene copolymers were compared to those of Hydrogenated Polybutadienes (HPB) reported by Krigas *et al*.[13] Such a comparison is depicted in Figure 4. Before proceeding further, it is important to note that HPBs are generally considered to be model random ethylene/1-butene copolymers, whose compositional homogeneity is ensured by the synthetic approach and can be accurately estimated. They are synthesized in a two-step process.[14,15,16] The first step involves the anionic polymerization of butadiene in cyclohexane. *s*-Butyllithum and dry isopropanol are used in the initiation and termination steps respectively. This results in the generation of a significant proportion of 1,2- or vinyl addition products, among other products formed. The proportion of the 1,2- product may be increased by the addition of polar modifiers into the polymerization medium.[17] The second step is the hydrogenation of the intermediate product using a Pd/$CaCO_3$ catalyst in cyclohexane solution. Upon hydrogenation, the polymer is converted into the equivalent of an ethylene/1-butene copolymer. This method of synthesis provides mild and uniform conditions for the growth of polymer chains. The resulting polymers are homogeneous in composition. Furthermore, the samples obtained are characterized by narrow molecular weight distributions ($M_w/M_n < 1.1$).

An examination of Figure 4 indicates that the two sets of data can be represented by a single curve, suggesting similarity in their sequence distribution. We therefore infer from these results that the ethylene/1-butene copolymers used in the present study have properties that approximate those expected from homogeneous and random copolymers.

Table 8 Bulk densities of ethylene/1-butene, ethylene/1-pentene and ethylene/1-hexene copolymers measured at 23°C (from L. Richardson)

Sample	Branch content (Mole %)	Time (days)	Density (g/ml)	Uncertainty (g/ml)
EB-928	1.45	60	0.9255	± 0.0002
EB-912	4.61	60	0.9121	± 0.0003
EB-894	8.97	60	0.9000	± 0.0001
EB-883	12.6	60	0.8850	± 0.0004
EB-879	13.7	60	0.8803	± 0.0003
EB-874	15.8	60	0.8758	± 0.0003
EP-910	4.44	30	0.9096	± 0.0004
EP-870	14.31	30	0.8765	± 0.0005
EH-910	3.60	30	0.9103	± 0.0002
EH-886	10.7	30	0.8854	± 0.0001
EH-869	14.2	30	0.8743	± 0.0008

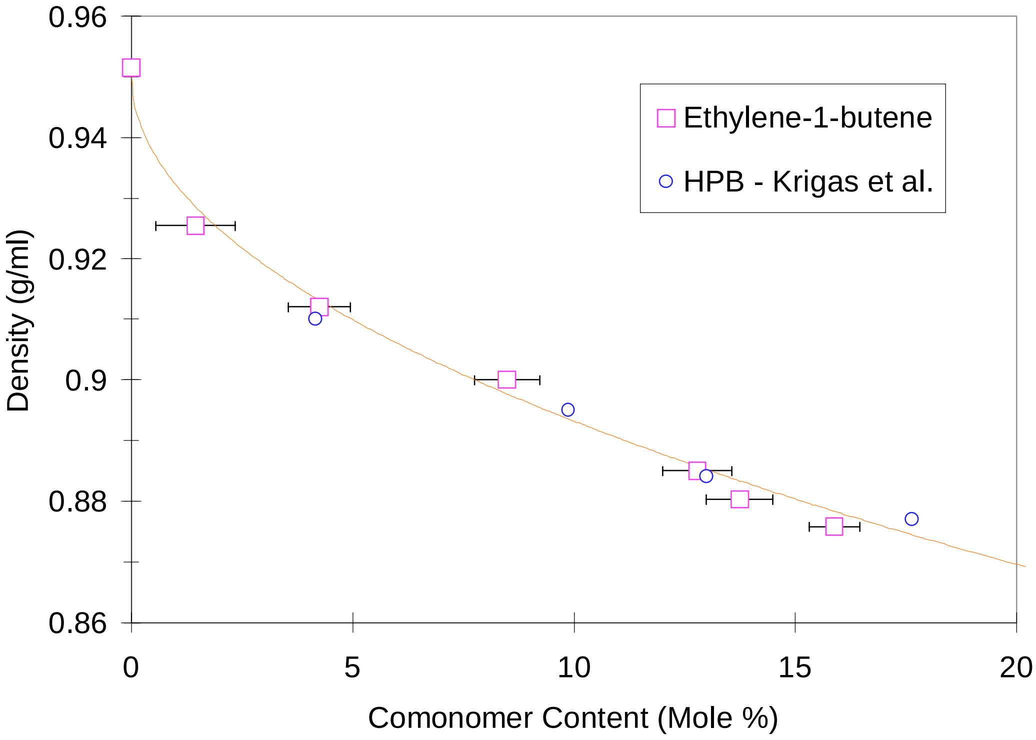

Figure 4 Comparison of the densities of ethylene/1-butene copolymers from the present study ( ) with the model hydrogenated polybutadienes from Krigas *et al*[13]. (❍). The value of comonomer content used is from Table 2.

The effect of residence time at 23°C on the bulk density of one of the ethylene/1-butene copolymers, EB-874 is shown in Figure 5. It is found that the density of the material continues to increase slowly with time, even at times as long as 10^5 min. However, the most significant increase in density occurs within the first 100-200 minutes. Identical observations are made from the crystallinity changes (changes in density are directly related to changes in the crystallinity of the samples) obtained via thermal analysis measurements as discussed in the next chapter.

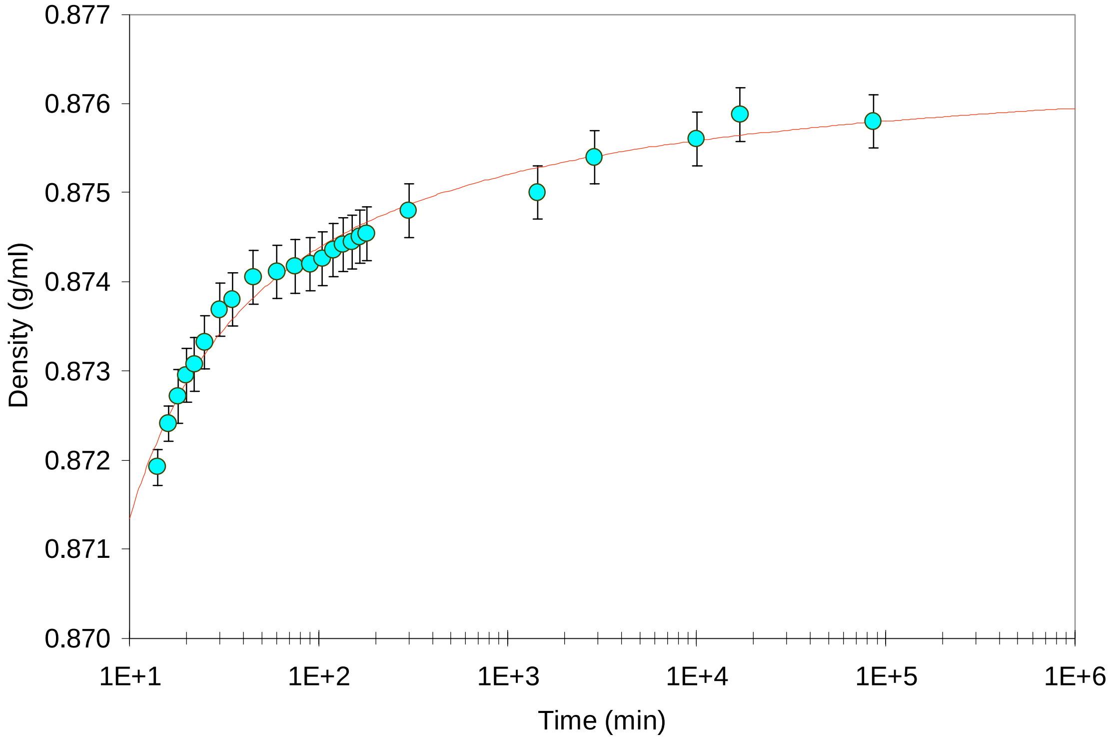

Figure 5 Effect of residence time at 23°C on the bulk density of EB-874
(from L. Richardson)

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