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Poly 1,3-butylene adipate Reoplex® as high molecular weight plasticizer for PVC-based cling films—microstructure and number-average molecular weight studied by ^{1}H and ^{13}C NMR

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Abstract

Reoplex® 346, a low number-average molecular weight ($\bar{M}_n$) poly 1,3-butylene adipate—frequently used as plasticizer in PVC-based cling-films—was studied by ^{1}H and quantitative ^{13}C NMR. It was found that Reoplex® results from the linear polyesterification of adipic acid (A) by an excess of butane 1,3-diol (B) with a (A/B) molar ratio of 0.88 giving a polyester having a number-average degree of polymerization ($\overline{\mathrm{DP}}_n$) and an absolute $\bar{M}_n$ of 15.7 and 1600 g/mol, respectively. As primary alcohol function is more reactive than secondary alcohol, Reoplex® chain-ends are made up of 28.6% of primary alcohol and 71.4% of secondary alcohol. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reoplex® 346; Plasticizer; Poly-1,3 butylene adipate

1. Introduction

Common plasticizers for thin PVC-based cling films—widely used for packaging foods—are typically diesters: di 2-ethyl hexyl adipate (DEHA) or di 2-ethyl hexyl phthalate (DEHP). Their specific migrations in organic solvents fat simulants have been studied [1–7].

Because of their low molecular weights (MW), DEHA [8] (MW = 370 g/mol) as well as DEHP [7] (MW = 390 g/mol) readily migrate into foods. In order to reduce the contamination of packaged foods, these low MW plasticizers may be—partially or totally—replaced by a low number-average molecular weight ($\bar{M}_n$) polyester, namely the poly butane 1,3-diol adipate or poly 1,3-butylene adipate (PBA—Reoplex® 346) [4,9,10].

To our knowledge, the actual physical chemical characteristics (diacid/diol molar ratio, rates of esterification, microstructure of the obtained polycondensate, etc.) of the commercial Reoplex® are not perfectly known, particularly its absolute $\bar{M}_n$ ($\bar{M}_{n,a}$). The present paper deals with its in-depth examination by ^{1}H and *quantitative* ^{13}C NMR in order to precisely determine its number-average degree of polymerization ($\overline{\mathrm{DP}}_n$) giving $\bar{M}_{n,a}$.

2. Experimental

Reagent: Reoplex® 346 (Ciba-Geigy) was used as purchased.

^{1}H and ^{13}C NMR spectrometry: For quantitative determinations using ^{1}H and ^{13}C NMR, and for (^{1}H/^{13}C) 2D NMR, spectra were recorded using a Bruker ARX 300 (300 and 75.5 MHz for ^{1}H and ^{13}C, respectively) and a Bruker DRX 400 (400.1 and 100.6 MHz for ^{1}H and ^{13}C, respectively) with Reoplex® samples dissolved in $CDCl_3$ or DMSO-d_6. Typical analysis conditions were as follows.

^{1}H (400 MHz) NMR: Concentration of Reoplex® 346 in $CDCl_3$ = 5% (w/v); temperature = 25°C; pulse angle = 30°; acquisition time = 2.7 s for 32k-words; sweep width = 6 kHz; delay = 2.3 s; number of scans = 16.

Quantitative ^{13}C (75.5 MHz) NMR: Concentration of Reoplex® 346 in $CDCl_3$ = 80% (w/v) in 10 mm NMR tube with about 40 mg of Cr acetylacetonate ($Cr(acac)_3$—relaxing agent); temperature = 25°C; pulse angle = 66°; acquisition time = 1.3 s for 32k-words; sweep width = 18.8 kHz; delay = 8 s; number of scans = 6000.

2D-Hetero-nuclear Multiple Quantum Coherence (HMQC) spectra were performed using a Bruker DRX 400 with a 5 mm inverse *Z*-gradient probe and a solution of Reoplex® in DMSO-d_6 at room temperature. Spectral widths: $F_2(^1H) = 2200$ Hz, $F_1(^{13}C) = 5330$ Hz. Time

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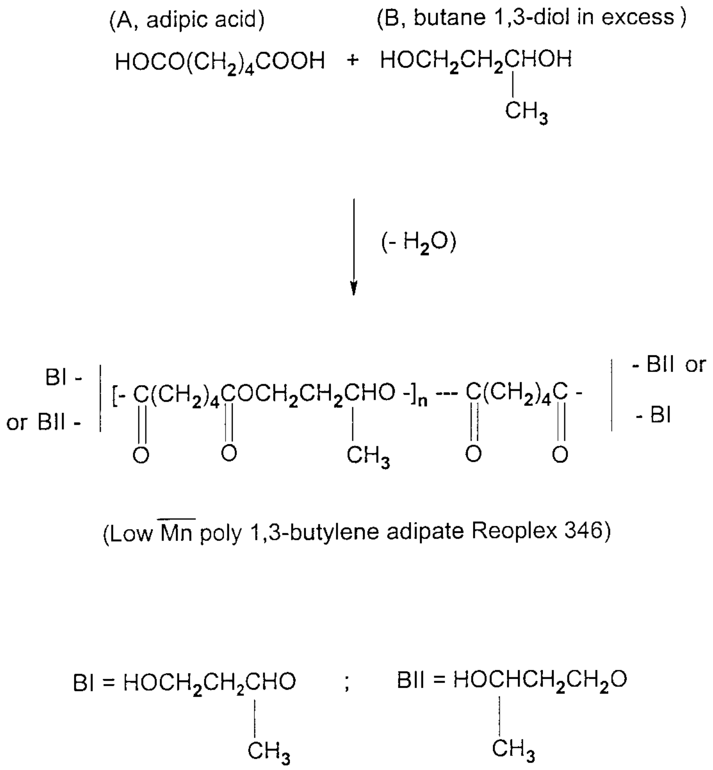


Scheme 1.

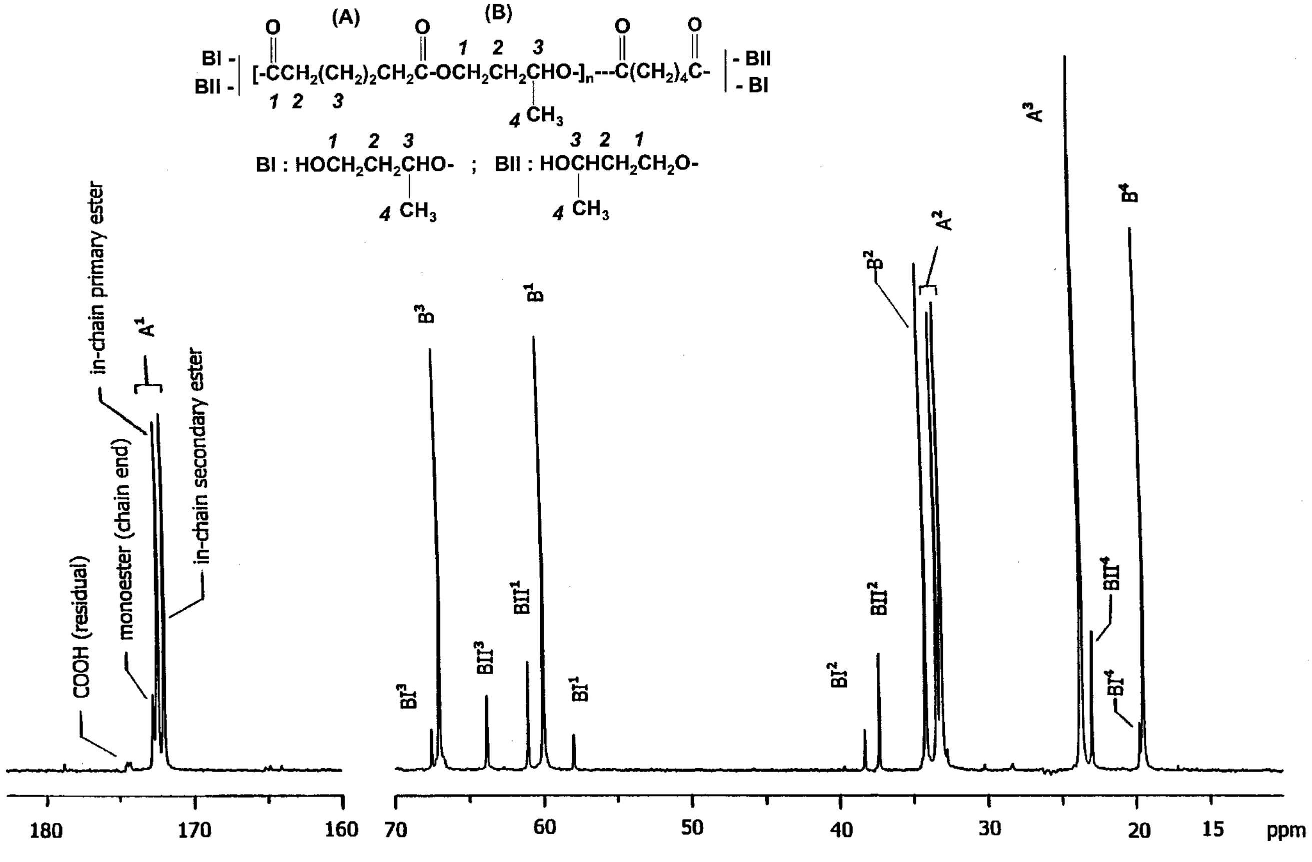


Fig. 1. Quantitative ^{13}C (75.5 MHz) NMR spectrum of low $\bar{M}_n$ poly 1,3-butylene adipate Reoplex® 346; solvent: $CDCl_3$; relaxing agent: $Cr(acac)_3$; room temperature.

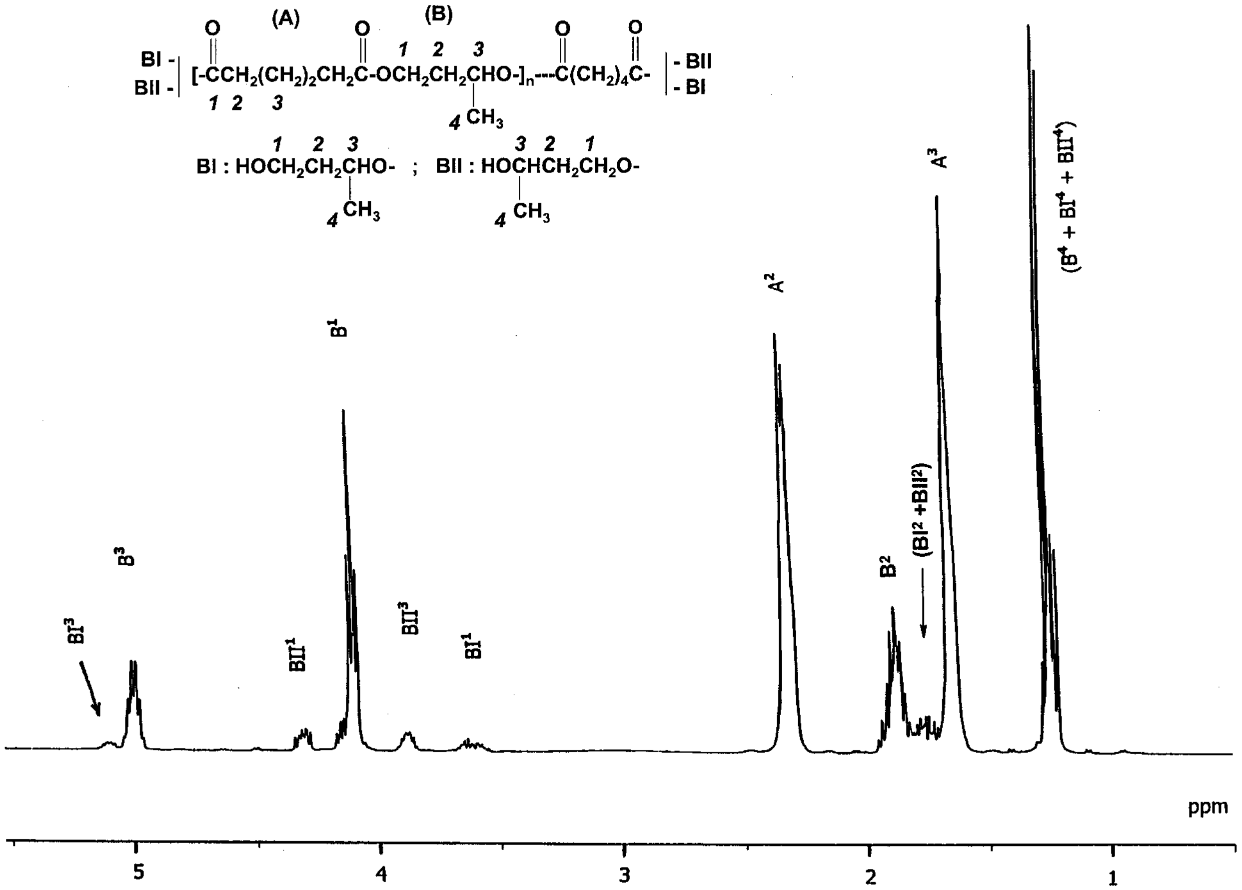


Fig. 2. ^1H (400 MHz) NMR spectrum of low $\bar{M}_n$ poly 1,3-butylene adipate Reoplex® 346; solvent: $CDCl_3$; room temperature.

domains: (^1H) = 1024 and (^{13}C) = 512; acquisition time (^1H) = 0.23 s; delay (^1H) = 2 s. Gaussian apodization was applied in both ^1H and ^{13}C domains.

3. Results and discussion

Because of its higher molecular weight (MW) or more precisely its higher number-average molecular weight ($\bar{M}_n$), poly 1,3-butylene adipate (PBA) plasticizer migrates less from cling films into packaged foods than the classical low MW diesters like di 2-ethyl hexyl adipate (DEHA; MW = 370 g/mol) [4,9,10] or di 2-ethyl hexyl phthalate (DEHP; MW = 390 g/mol). Commercial PBA or Reoplex® 346—synthesised by polyesterification in bulk of adipic acid (A) with an excess of butane 1,3-diol (B) is a stable linear low $\bar{M}_n$ polyester having two expected hydroxyl chain-ends (more stable than acid ends) (Scheme 1).

By Size Exclusion Chromatography (SEC) with polystyrene standards, $\bar{M}_n$ (SEC) and $\bar{M}_w$ (SEC) (weight-average molecular weight) of Reoplex® equal 1950 and 4000, respectively [10,11]. To our knowledge, only one published paper [10] deals with some physical characteristics of Reoplex®: its (i) fractionation in seven fractions using preparative SEC; and (ii) partial examination by ^1H NMR and estimation of the MWs ($\bar{M}_n$s, more properly) of the six first isolated fractions.

In the present quantitative study of Reoplex®, intensive use of ^1H, quantitative ^{13}C NMR and $^1H/^{13}C$-two dimension (2D) HMQC (Hetero-nuclear Multiple Quantum Coherence) NMR permits the assignment of all the ^1H and ^{13}C resonance peaks, thus the easy calculations of: (i) the A/B molar ratio; (ii) the individual rates of esterification of the primary and secondary alcohol functions of B as well as its overall rate of esterification (the completion of esterification of acid groups of A may be verified by ^{13}C NMR) hence (iii) the actual number average degree of polymerization ($\overline{DP}_n$) and the corresponding $\bar{M}_{n,a}$.

3.1. NMR spectrometry

^1H and ^{13}C NMR spectra of high $\bar{M}_n$ poly alkyl diol adipates are relatively well known [12]. The present case deals with a low $\bar{M}_n$ PBA and, because of the high proportions of primary (BI) and secondary (BII) alcohol chain-ends (Scheme 1), its ^{13}C (Fig. 1) and ^1H (Fig. 2) spectra are more complex, particularly in the (55–70 ppm) and (170–175 ppm) regions of ^{13}C and the (1.7–1.8 ppm) and (3.5–5.3 ppm) regions of ^1H resonances. Precise assignments of all these ^1H and ^{13}C resonances require (^1H, ^1H)

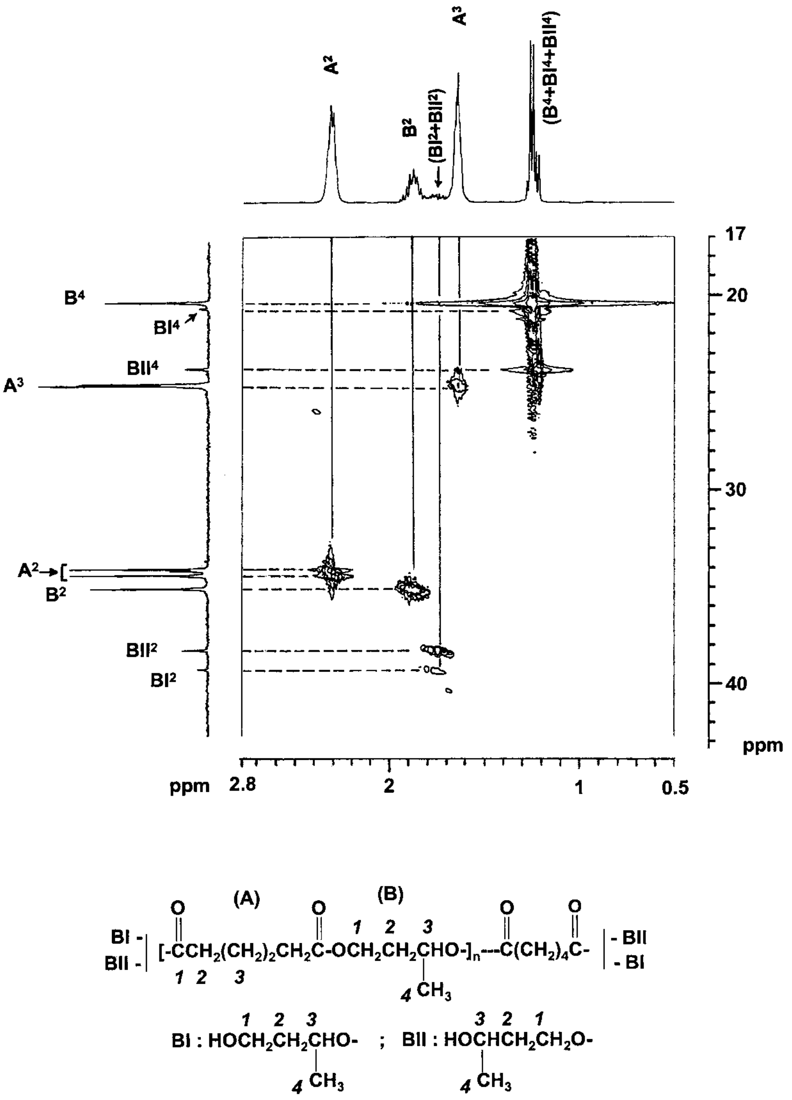


Fig. 3. ^{1}H/^{13}C HMCQ spectrum of low $\bar{M}_n$ poly 1,3-butylene adipate Reoplex® 346; solvent: DMSO-d$_6$; room temperature. Enlargement of the (^{1}H, 1.5–2.5 ppm) and (^{13}C, 32–41 ppm) domains.

decoupling experiments, 135° ^{13}C DEPT (Distorsionless Enhancement by Polarisation Transfer) and ^{1}H/^{13}C-HMQC spectra (Figs. 3 and 4).

3.1.1. *Quantitative ^{13}C NMR spectrum (Fig. 1)*

Of interest is the observation that only traces of COOH are found at 174.4 ppm. The polyesterification in bulk of the (aA + bB, $b > a$) mixture is actually almost complete. This important information cannot be obtained by ^{1}H NMR.

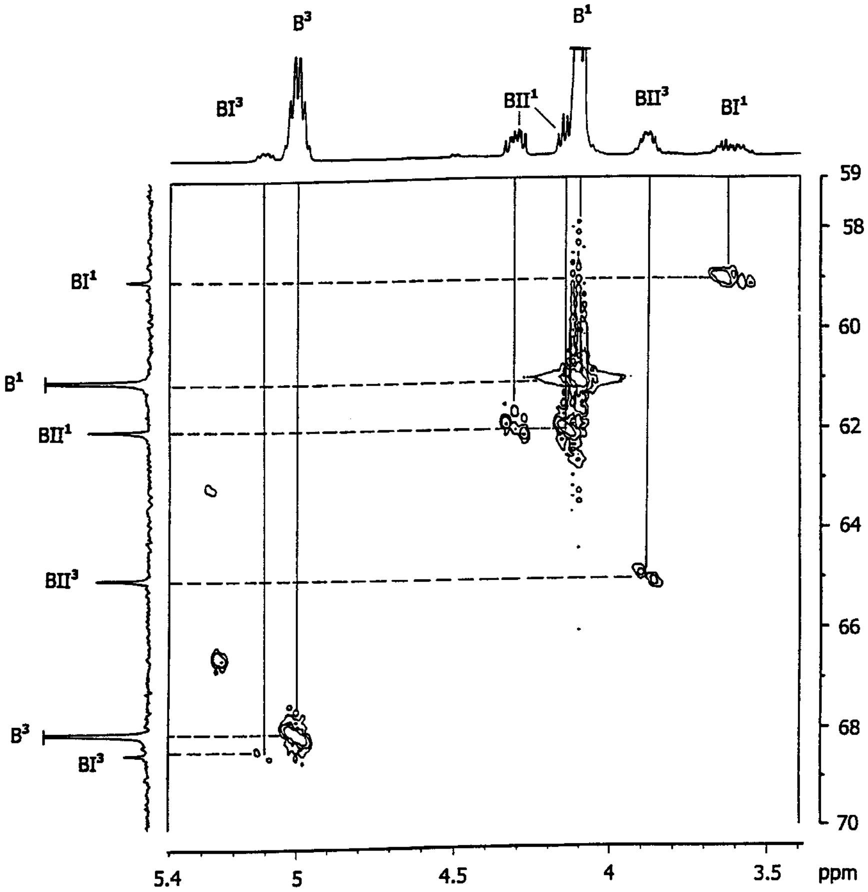
For in-chain A-units, compared to known ^{13}C NMR spectra of poly alkyl-diol adipates [12; p. 169,171,173], here the classes of esters' functions—primary (BII) and secondary (BI) esters—affect the δ-values of both A^{1} (2CO) and A^{2} (2CH$_2$). Each one of them splits into two lines: 172.0 and 172.4 ppm for A^{1}, 33.0 and 33.4 ppm for A^{2} (Figs. 1 and 3). Only the remote central A^{3} (2CH$_2$) remains unaffected at 23.6 ppm.

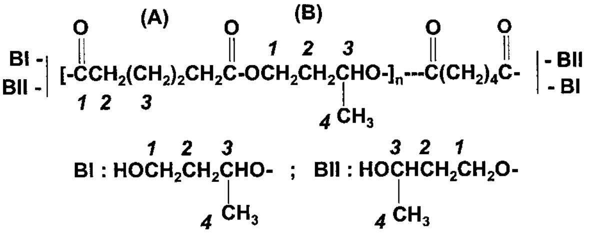
Taking into account the smaller proportion of secondary ester BI^{3} (secondary alcohol is known to be less reactive than primary alcohol) the smallest CO-ester line at 172.8 ppm should be assigned to the carboxy A^{1} group linked to BI chain-end (A^{1}-BI sequence). The stronger CO resonance of the primary ester of the A^{1}-BII sequence should be overlapped by the two strongest in-chain A^{1}-carboxy lines (172.0; 172.4 ppm).

The better ^{13}C NMR spectral resolution allows the discrimination of all the four couples of lines of BI and BII chain-ends (Figs. 1 and 3). The BII/BI molar ratio may easily be deduced by comparing the relative intensities of BII^{1} (61.0 ppm), BII^{3} (63.8 ppm) and BII^{2} (37.3 ppm) to those of BI^{1} (57.9 ppm), BI^{3} (67.5 ppm) and BI^{2} (38.2 ppm), respectively (Figs. 1 and 4).

3.1.2. *^{1}H NMR spectrum (Fig. 2)*

The strongest ^{1}H resonances of in-chain A and B units are easily identified. The two unresolved wide resonances





$$\begin{matrix}BI-\\BII-\end{matrix}\left[-\overset{O}{\overset{\|}{C}}CH_2(CH_2)_2CH_2\overset{O}{\overset{\|}{C}}-OCH_2CH_2\underset{CH_3}{\underset{|}{C}}HO-\right]_n---\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-\begin{matrix}-BII\\-BI\end{matrix}$$

$$BI: HOCH_2CH_2\underset{CH_3}{\underset{|}{C}}HO- \;;\; BII: HO\underset{CH_3}{\underset{|}{C}}HCH_2CH_2O-$$

Fig. 4. $^1H/^{13}C$ HMCQ spectrum of low $\bar{M}_n$poly 1,3-butylene adipate Reoplex® 346; solvent: DMSO-d_6; room temperature. Enlargement of the (^1H, 3.4–5.4 ppm) and (^{13}C, 59–70 ppm) domains.

centred at 1.654 and 2.320 ppm belong to A^3 (4H) and A^2 (4H), respectively [12; p. 170,172,174]. The two esterified primary B^1 (2H, triplet) and secondary B^3 (1H, sextet) alcohol-ends are found at 4.10 and 5.00 ppm, respectively. Finally, the two central B^2 protons resonate around 1.90 ppm (CH_2, unresolved multiplet), and those of the in-chain methyls B^4 (strongest doublet) at 1.262 and 1.246 ppm.

The presence of monoesterified BI (primary alcohol end) and BII (secondary alcohol end) give rise to new ^1H and ^{13}C resonances that may only be assigned by $^1H/^{13}C$-2D HMQC NMR spectra (Figs. 3 and 4). As previously stated ($BI^3 < BII^1$), the intensities of the BI ^1H resonances are logically expected to be smaller than those of the BII's ones.

Compared to the $\delta(^1H)$-values of in-chain B resonances—because of the presence of methylene—(BI^1—unresolved multiplet due to the overlapping of CH_2 and OH resonances; $\delta = 3.6$ ppm) and methine—(BII^3—sextet; $\delta = 3.90$ ppm) alcohol ends—the two corresponding ester groups BI^3 (1H sextet) and BII^1 (2H unresolved multiplet) undergo downfield shifts and resonate at 5.12 and 4.30 ppm, respectively. In contrast, the resonances of their central methylenes—BI^2 and BII^2—shift to higher fields, at around 1.75 ppm. The doublet of the BII^4-methyl protons appears at 1.216 and 1.232 ppm, at slightly higher field than that of the in-chain methyls B^4. Finally, only one line of the BI^4-methyl proton doublet is visible at 1.279 ppm, the second one being overlapped by the strongest in-chain B^4-methyl doublet (Fig. 3).

As previously, the BII/BI molar ratio (or (secondary

Table 1
Microstructure of Reoplex® 346 (poly butane 1,3-diol adipate) studied by ^{1}H and quantitative ^{13}C NMR. Individual rates of esterification of primary (EI %) and secondary (EII %) alcohol functions and overall rate (EB %) of esterification of butane 1,3-diol (B) in excess by adipic acid (A) in bulk. A/B: (adipic acid/butane 1,3-diol) molar ratio ($r < 1$).$\overline{\mathrm{DP}}_\mathrm{n}$: number-average degree of polymerisation

	EI(%)	EII(%)	EB(%)	r = A/B	$\overline{\mathrm{DP}}_\mathrm{n}$
Eq. no.	(3)	(4)	(5)	(6)	(7)
^{1}H NMR	93.1	82.3	87.8	0.878	15.4
^{13}C NMR	93.1	83.3	88.2	0.882	15.9

alcohol-end/primary alcohol-end) ratio) may be easily calculated by comparing the relative intensity of BII^3 (1H) to that of BI^3 (1H) and cross-checked by quantitative ^{13}C NMR.

3.1.3. Quantitative determinations

The BII/BI ratio may be easily calculated by ^{1}H [$(\mathrm{BII/BI})_\mathrm{H}$—Fig. 2, Eq. (1)] or ^{13}C [$(\mathrm{BII/BI})_\mathrm{C}$—Fig. 1, Eq. (2)] NMR as following:

$$\left(\frac{\mathrm{BII}}{\mathrm{BI}}\right)_H = \frac{\mathrm{BII}^3}{\mathrm{BI}^3} \tag{1}$$

$$\left(\frac{\mathrm{BII}}{\mathrm{BI}}\right)_\mathrm{C} = \frac{\mathrm{BII}^1}{\mathrm{BI}^1} = \frac{\mathrm{BII}^3}{\mathrm{BI}^3} = \frac{\mathrm{BII}^2}{\mathrm{BI}^2} \tag{2}$$

BI^1, BI^2, BII^1, etc. are the corresponding ^{1}H or ^{13}C relative intensities.

Within experimental errors, one has:

BII/BI = secondary alcohol-end/primary alcohol-end = 2.5 ± 0.1

Thus, in the present polyesterification in bulk of adipic acid A by an excess of butane 1,3-diol B, the (primary ester-end/secondary ester-end) ratio (= $\mathrm{BII}^1/\mathrm{BI}^3$) amounts to 2.5 or, in other words, the primary alcohol function is 2.5 times more reactive than the secondary one.

The individual rates of esterification of primary (EI %) and secondary (EII %) and the overall (EB %) rate of esterification are given by Eqs. (3)–(5).

$$\mathrm{EI}\% = \frac{(\mathrm{B}^1 + \mathrm{BII}^1) \times 10^2}{\mathrm{B}^1 + \mathrm{BII}^1 + \mathrm{BI}^1} \tag{3}$$

$$\mathrm{EII}\% = \frac{(\mathrm{B}^3 + \mathrm{BI}^3) \times 10^2}{\mathrm{B}^3 + \mathrm{BI}^3 + \mathrm{BII}^3} \tag{4}$$

$$\mathrm{EB}\% = \frac{(\mathrm{EI}\% + \mathrm{EII}\%)}{2} \tag{5}$$

B^1 and B^3 are the relative intensities of the corresponding in-chain ester groups $\mathrm{CH_2O}$ and CHO.

The esterification of A being almost complete, the r = A/B molar ratio equals (Eq. (6)):

$$r = \mathrm{A/B} = \mathrm{EB} \times 10^{-2} \tag{6}$$

All the values calculated by using Eqs. (3)–(6) are reported in Table 1.

3.2. Number-average degree of polymerization ($\overline{\mathrm{DP}}_\mathrm{n}$) and absolute number-average molecular weight ($\bar{M}_\mathrm{n,a}$)

Reoplex® chains, resulting from the linear polyesterification in bulk of A by an excess of B and bearing two hydroxyl ends, may statistically be represented as following.

BI(or BII)ABA…ABABII(or BI)

Here, with $r = 0.88 \pm 0.002 (<1)$, the maximum value of $\overline{\mathrm{DP}}_\mathrm{n}$ reached at complete esterification of A (only traces of COOH were found around 174.5 ppm (Fig. 1)) is given by Eq. (7) [13] (Table 1):

$$\overline{\mathrm{DP}}_\mathrm{n} = \frac{1 + r}{1 - r} = 15.7 \pm 0.3 \tag{7}$$

(DP = 1 corresponds to A or B monomer)

The polydispersity index (= 1 + r) amounts to near 1.9.

For a given value of $\overline{\mathrm{DP}}_\mathrm{n}$, the corresponding number of esterification reactions equals ($\overline{\mathrm{DP}}_\mathrm{n} - 1$). Thus Reoplex® results from the polyesterification in bulk of

- $\left(\frac{\overline{\mathrm{DP}}_\mathrm{n} - 1}{2} + 1\right)$ B monomer units by
- $\left(\frac{\overline{\mathrm{DP}}_\mathrm{n} - 1}{2}\right)$ A monomer units

with the loss of ($\overline{\mathrm{DP}}_\mathrm{n} - 1$) moles of $\mathrm{H_2O}$, consequently its $\bar{M}_\mathrm{n,a}$ may be easily calculated (Eq. (8)):

$$\bar{M}_\mathrm{n,a} = \frac{\overline{\mathrm{DP}}_\mathrm{n} - 1}{2} \times \mathrm{MW}(A) + \left(\frac{\overline{\mathrm{DP}}_\mathrm{n} - 1}{2} + 1\right) \times \mathrm{MW}(B) - (\overline{\mathrm{DP}}_\mathrm{n} - 1) \times \mathrm{MW}(\mathrm{H_2O}) \tag{8}$$

with MW(A) = 146.14 g/mol, MW(B) = 90.12 g/mol and $\mathrm{MW(H_2O)}$ = 18 g/mol, one gets:

$$\bar{M}_\mathrm{n,a} = 100.13\ \overline{\mathrm{DP}}_\mathrm{n} - 10.01 \tag{9}$$

hence $\bar{M}_\mathrm{n,a}$ (Reoplex®) = 1562 ± 20 g/mol.

As usually observed, here the value of $\bar{M}_\mathrm{n,a}$ calculated by ^{1}H and quantitative ^{13}C NMR is smaller than that found by SEC (= 1900 g/mol) using polystyrene standards [10,11].

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