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# Characterization of Poly(ethyleneoxyethylene terephthalate-*co*-adipate) using NMR Spectroscopy

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Comonomer sequence distribution and $^1$H-NMR chemical shifts were determined for poly(ethyleneoxyethylene terephthalate-*co*-adipate) (PEOETA) copolyester. The sequence distribution of terephthalate (T) and adipate (A) residues was found to be random, which is typical for copolyesters synthesized via bulk polycondensation. The inner methylene protons of EOE residues appeared as a pair of doublets due to chemical shift differences among the EOE-centered dyad sequences TT, TA, AT, and AA. The four equivalent phenylene protons of T residues appeared as a triplet due to chemical shift differences among the T-centered triad sequences TTT, TTA (=ATA), and ATA. Higher-order tetrad and pentad sensitivity were also observed for the inner methylene and phenylene protons, respectively, especially for TT- and TTT-centered sequences. The sequence sensitivity of the phenylene protons was attributed to unique spatial interactions between themselves and protons within adjacent adipate and EOE units. These spatial interactions were confirmed using Nuclear Overhauser Enhancement Spectroscopy (NOESY).

**Keywords:** PEOETA; poly(ethyleneoxyethylene terephthalate-*co*-adipate); NMR spectroscopy; aromatic-aliphatic copolyester; sequence distribution; spatial interactions

## 1 Introduction

The use of biodegradable polymers in consumer products has grown in the past decade due to the emergence of cost–effective, aromatic-aliphatic copolyesters (AAC). These polymers are typically produced from a mixture of terephthalic and adipic acids, along with a simple aliphatic diol such as ethylene, butylene, and/or ethyleneoxyethylene. The aromaticity of the copolyesters imparts good physical properties while the aliphatic moieties provide a pathway of degradation. Two commercially available AACs are Eastar Bio® and Ecoflex® produced by Eastman and BASF, respectively.

In the course of synthesizing A-B-A block copolyesters (1), where the middle block (B) is an AAC and the outer blocks (A) are poly(L-lactide), we found that a particular AAC, poly(ethyleneoxyethylene terephthalate-*co*-adipate) (PEOETA) displays a unique sensitivity of the terephthaloyl protons toward diacid comonomer sequence, as observed by nuclear magnetic resonance (NMR) spectroscopy. Upon examination of the $^1$H-NMR spectrum it was discovered that a splitting occurs in the aromatic region, which has not been observed in previous studies of ACCs containing terephthoyl and adipoyl units (2, 3) and moreoever, would not be predicted due to the well-known insensitivity of $^1$H-NMR spectroscopy toward long-range effects. We further concluded that the observed splitting was not due to the presence of dissimilar diol units, which might arise from impure diethylene glycol staring material or premature degradation of the copolyester. Supporting this conclusion is the fact that the $^1$H-NMR spectrum of poly(ethylene/butylene terephthalate) exhibits only one peak representing the four protons of the aromatic ring of the terephthaloyl units (4). Subsequently, we have determined by 2D-NMR techniques that the splitting arises from spatial interactions of the aromatic ring protons with neighboring EOE and adipate units. These through-space interactions, which to our knowledge have not been previously reported, are thought to arise from the conformations created by the use of diethylene glycol in a polyester containing both terephthalate and adipate units.

$^1$H-NMR spectroscopy has been previously used to determine the distribution of terephthalate (T) and adipate (A) units within poly(butylene terephthalate-*co*-adipate) (PBTA), in terms of the butylene (B)-centered sequences TBT, ABA, and ABT (=TBA) (2). In this study, we have similarly determined the sequence distribution of PEOETA, using the methylene proton resonance signals of the EOE

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units. In analogy to the definition of stereo sequences in vinyl polymers, we have defined such diacid-EOE-diacid sequences as a "dyad" and represented the four possible sequences within PEOETA as TT, TA (=AT), and AA. We have also identified and assigned multiple aromatic proton signals arising from dissimilar terephthalate-centered triads, ATA, TTA (=ATT), and TTT.

## 2 Experimental

### 2.1 Materials

Dimethyl adipate (99+%), dimethyl terephthalate (99%), diethylene glycol (DEG, 99%) (Acros Organics) and FASTCAT 4100 (Atofina) were used as received.

### 2.2 Polyester Synthesis

Polyesters were produced using a 4-necked 250 mL round-bottom flask equipped with a magnetic stirrer, nitrogen gas inlet tube, thermometer, and distillation head for removal of reaction by-products. The following synthesis procedure for PEOETA is representative. To the flask were charged 78.88 g (0.513 mole) dimethyl terephthalate, 74.54 g (0.171 mole) dimethyl adipate, 101.79 g (0.787 mole) diethylene glycol and 0.10 g (0.05% w/w of total polymer) of FASCAT 4100 (catalyst). Under nitrogen, the mixture was slowly heated with stirring until all components became molten (150–170°C). Heating and stirring were continued and methanol was continuously distilled as the transesterification reaction proceeded. When no further methanol could be removed under atmospheric pressure, a slight vacuum (100 mm Hg) was applied until the theoretical amount of methanol had been approximately collected. The vacuum was then gradually increased until a final vacuum of 0.200 mm Hg was achieved. The reaction was kept under these conditions, and molecular weight of the final polyester was controlled by careful removal of a theoretical amount of DEG. When the targeted amount of DEG had been collected, heating was discontinued and the contents were allowed to cool to ~100°C under nitrogen flow. The molten polymer was then carefully poured into a receiving vessel and cooled to room temperature.

Following the above procedure PEOETA-50, PEOETA-25, PEOETA-75, PEOET and PEOEA polyesters were synthesized. The 25, 50, and 75 denote the terephthalate mole percentage in the co-diacide feed. The number average molecular weights ($M_n$), molecular weight distributions (MWD) and glass transition temperatures ($T_g$) of the polyesters discussed herein are listed in Table 1.

**Table 1.** Number average molecular weight ($\bar{M}_n$), molecular weight distribution (MWD) and $T_g$ (DSC) of polyesters

| Copolyester | $\bar{M}_n$ (g/mol) | MWD | $T_g$ (°C) |
|---|---|---|---|
| PEOETA-50 | 8,600 | 1.25 | −28 |
| PEOETA-25 | 9,200 | 1.29 | −40 |
| PEOETA-75 | 18,600 | 1.49 | −4.4 |
| PEOET | 7,600 | 1.45 | 16 |
| PEOEA | 8,300 | 1.64 | −49 |

Procedure for Mn and MWD determination is described in Ref. 1. Tg was obtained using a TA Instruments Q1000 differential scanning calorimeter (DSC) at a heating rate of 10°/min within a temperature range of −50°C to 100°C.

### 2.3 Instrumentation

Solution $^1$H-NMR spectra were obtained on a Varian Unity 500 MHz spectrometer at 25°C (unless otherwise stated) using 5 mm o.d. tubes with sample concentrations of 5–7% (w/w) in deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulfoxide (*d*-DMSO) (Aldrich Chemical Co.) containing tetramethylsilane as an internal reference. The *d*-DMSO was employed only in the variable temperature studies due to its higher thermal stability and boiling point. Chemical shifts were referenced from the TMS signal taken at 0.0 ppm. $^1$H spin-lattice relaxation times ($T_1$) were determined using an inversion-recovery pulse sequence (180°-$\tau$-90°) with a delay of 20 s between scans.

Nuclear Overhauser Enhancement SpectroscopY (NOESY) experiments were performed using a delay time

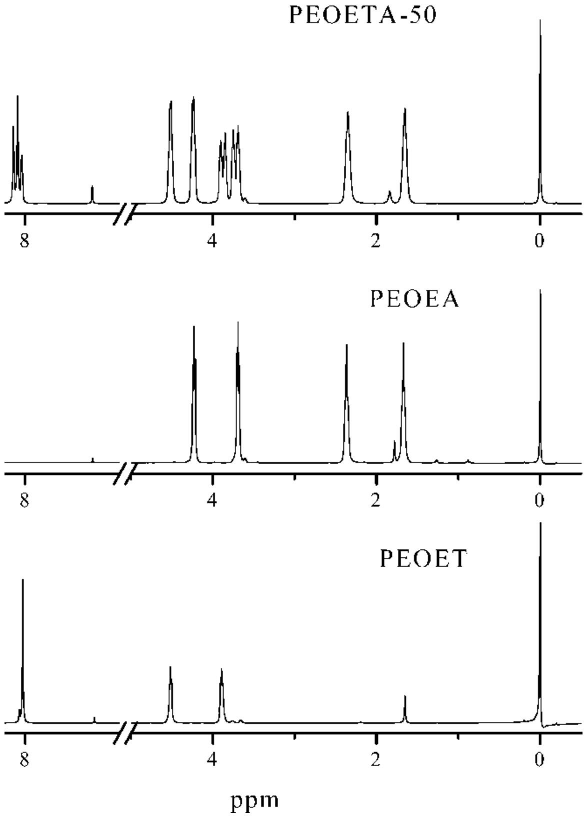

**Fig. 1.** $^1$H-NMR spectra of copolyester (PEOETA) and polyesters PEOEA and PEOET.

of 2 × $T_1$, obtaining 200 increments and 16 scans per increment, within a spectral width of 4000 Hz.

## 3 Results and Discussion

The proton NMR spectrum of PEOETA-50 copolyester is shown in Figure 1; for comparison the spectra of PEOEA and PEOET homopolyesters are also depicted.

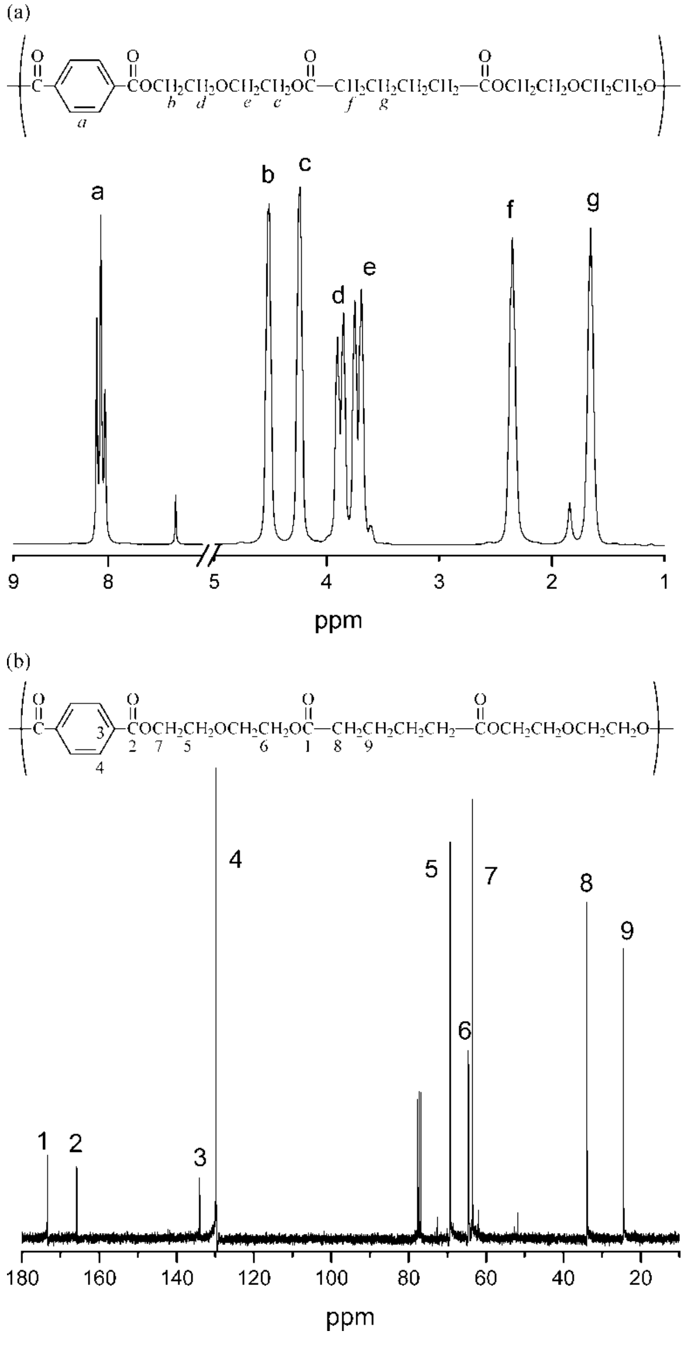

**Fig. 2.** (a) Peak assignments of the proton resonance signals of PEOETA copolyester; (b) Peak assignments of the carbon resonance signals of PEOETA copolyester.

The complete carbon and proton resonance assignments of PEOETA-50 copolyester are specified in Figures 2a and 2b.

As shown in Figure 2a, the aromatic protons (*a*) of PEOETA-50 copolymer appear as a triplet. This was unexpected since at least 12 covalent bonds separate a given aromatic proton from the nearest diacid structural unit. Furthermore, the terephthalate proton signal appears as a singlet in poly(butylene terephthalate-*co*-adipate) (PBTA) and poly(ethylene terephthalate-*co*-adipate) (PETA) copolyesters (2, 3). The observed splitting cannot be due to structural variations in the diol units caused by impurities or side reactions, since the spectral region associated with the diol units in PEOETA-50, PEOEA and PEOET (Figure 1) shows no extraneous peaks. Additionally, if degradation of the diethylene glycol units to ethylene glycol was the cause of the unique splitting in PEOETA-50, one would also see similar splitting in the PEOET polyester, yet no such splitting is observed in the $^1$H-NMR spectrum of PEOET (Figure 1). The splitting of the aromatic region shows no observable changes (Figure 3) upon heating of the copolyester in solution (*d*-DMSO) during $^1$H-NMR experiments, except for chemical shift anisotropy effects (5). Persistence of the splitting phenomenon at higher temperatures suggests that splitting does not originate from slow exchange between different rotational states of the phenylene ring, but rather, the latter is a free rotor (6).

Heteronuclear Single Quantum Correlation spectroscopy (HSQC) experiments (Figure 4) showed that the aromatic protons associated with the triplet are attached to four identical aromatic carbons ($C_4$ in Figure 2b). Therefore, the splitting must originate from through-space interactions of the aromatic protons with protons contained within or closely

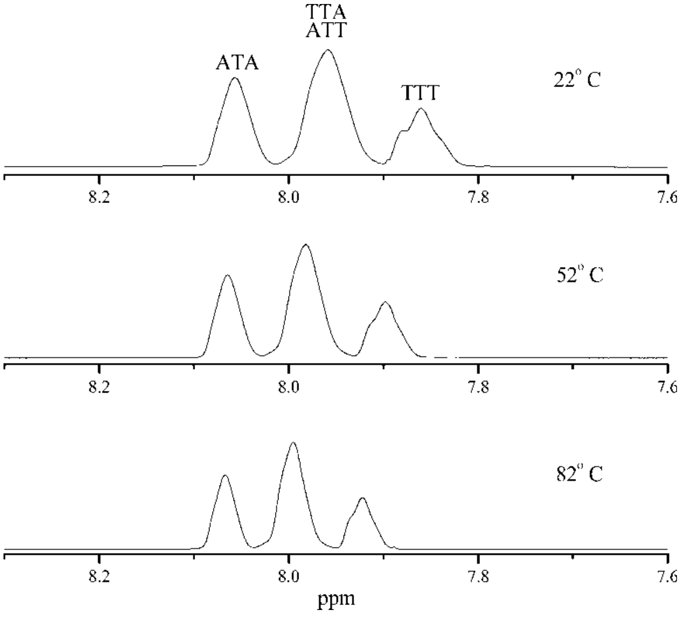

**Fig. 3.** $^1$H-NMR spectra displaying aromatic region of PEOETA at varying temperatures with triad sequences labeled.

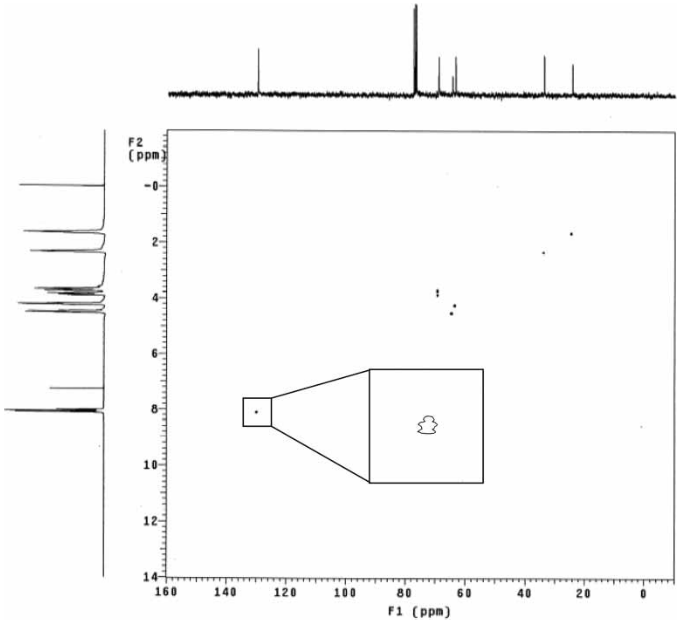

**Fig. 4.** 2D-HSQC spectrum of PEOETA displaying magnification of cross peak of aromatic unsubstituted carbons of terephthalate unit and *a*. (128 increments, 16 scans per increment and a delay time of 4 s.).

associated with nearest-neighbor diacid units. The relative intensities of the three aromatic proton peaks as a function of copolyester composition (Figure 5) allowed assignment of the peaks to the four identical protons within each of the terephthalate-centered triads as follows: ATA ($a_1$, 8.12 ppm), ATT and TTA ($a_2$, 8.08 ppm), and TTT ($a_3$, 8.03 ppm). Close inspection of the TTT proton peak ($a_3$) revealed further higher-order sensitivity to sequence distribution, namely pentad sensitivity as tentatively assigned in Figure 6.

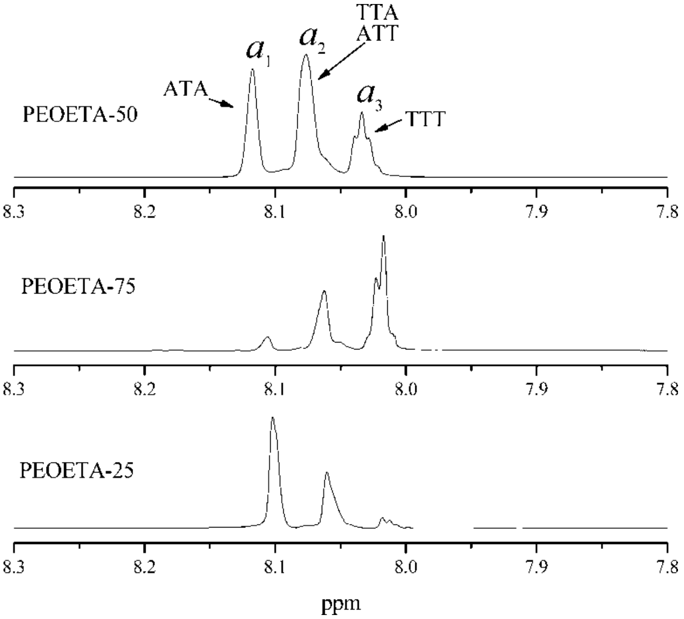

**Fig. 5.** Expansion of aromatic region of PEOETA-50, PEOETA-75 and PEOETA-25 showing triad sequence labels.

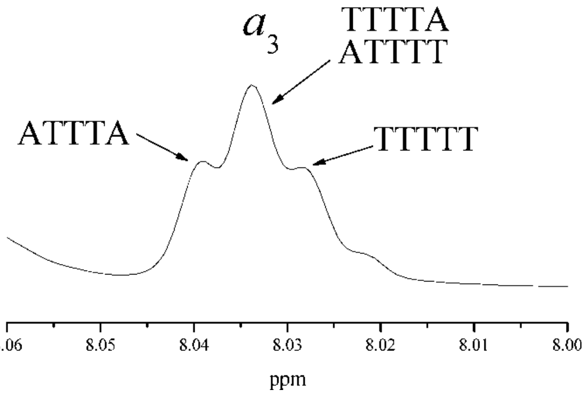

**Fig. 6.** Proton resonance peak $a_3$ with pentad sequences labeled.

We used a NOESY pulse sequence to resolve the identity of the protons involved in the through-space interactions. The $\tau_m$ chosen for the NOESY experiment was 800 ms, with a delay time of $2 \times T_1$ of *a*. $T_1$ relaxation times of aromatic and methylene protons are listed in Table 2.

The NOESY spectrum in Figure 7 reveals the existence of interactions that are responsible for the unique splitting of the aromatic protons. The expanded region of Figure 7 shows connectivity between the aromatic protons (*a*) and methylene protons *b*, $d_1$, $d_2$, and $e_1$ of the EOE units and *f* and *g* of the adipate units. This information was used to construct Figure 8, which shows the specific methylene protons associated with the central aromatic protons of each terephthalate-centered triad sequence. For example, the central aromatic protons ($a_3$) of a TTT pentad are associated only with *b* and $d_1$ protons, since only these protons are proximate to the central aromatic ring. Likewise, it is perfectly sensible that $e_2$ protons are not associated with any of the three types of aromatic protons, since the former exist only between two consecutive adipate residues.

Additional NOESY experiments using $\tau_m$s between 200 and 700 ms revealed a nuclear Overhauser enhancement (nOe) for only the methylene protons *b*. This is conceivably due to the fact that the *b* protons are spatially closer to the *a* protons than the other methylene protons. The occurrence of the nOe between the *b* and *a* protons is to be expected, as described in the research performed by Spera and coworkers (7). They were able to add an additional constraint to the conformation of PET, as originally determined by

**Table 2.** $T_1$ relaxation times for selected $^1$H

| $^1$H | $T_1$(s) |
|---|---|
| *a* | 1.36 |
| *b* | 0.51 |
| $d_{1,2}$; $e_{1,2}$ | 0.43; 0.62 |

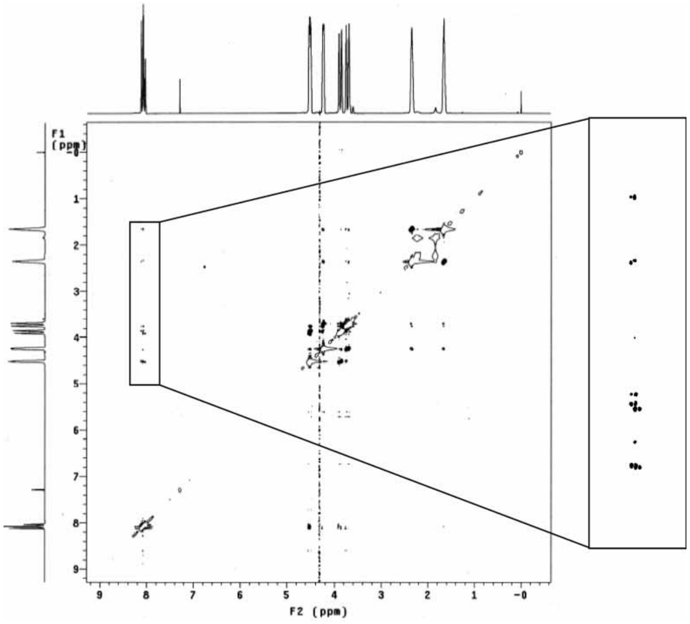

**Fig. 7.** 2D-NOESY spectrum of PEOETA copolyester showing magnification of $a$, $d_1$, $d_2$, $e_1$, $e_2$, $f$, and $g$.

Štokr and coworkers (8), which set the aromatic ring in a *cis* conformation about the ArCO-O bond. The exact conformations of the EOE and adipate units of PEOETA-50 that led to the observed interactions is still in question and further NMR and IR studies will be necessary for a complete understanding of this phenomenon.

The inner methylene proton signals arising from the EOE units of PEOETA-50 copolyester have chemical shifts at 3.68, 3.74, 3.84, and 3.89 ppm. These peaks are associated with the four EOE-centered dyads AA ($e_2$), AT ($e_1$), TA ($d_2$), and TT ($d_1$), respectively. Figure 9 shows an expansion of this region of the $^1$H-NMR spectrum for PEOETA copolyesters PEOETA-25, PEOETA-50, and PEOETA-75.

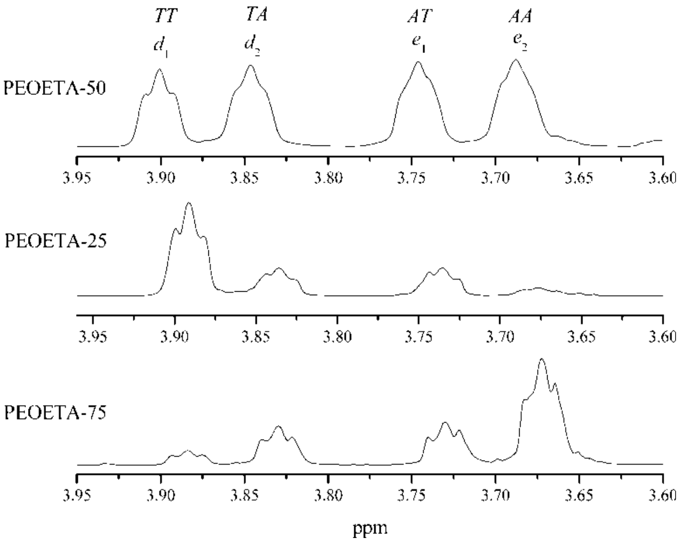

**Fig. 9.** Expanded $^1$H NMR spectra showing inner methylene proton signals of EOE units of PEOETA copolyesters with dyads labeled.

The fractions of adipate and terephthalate residues in the copolymer, $X_A$ and $X_T$ respectively, were calculated using Equations (1) and (2),

$$X_A = \frac{A_{AA} + A_{AT}}{A_{AA} + A_{AT} + A_{TT} + A_{TA}} \quad (1)$$

$$X_T = 1 - X_A = \frac{A_{TT} + A_{TA}}{A_{TT} + A_{TA} + A_{AA} + A_{AT}} \quad (2)$$

where $A$ equals the area obtained by integrating the peaks associated with the respective dyads. The probability ($P$) of finding a terephthalate unit next to an adipate unit can be calculated by Equation (3).

$$P_{TA} = \frac{A_{TA}}{A_{TA} + A_{TT}} \quad (3)$$

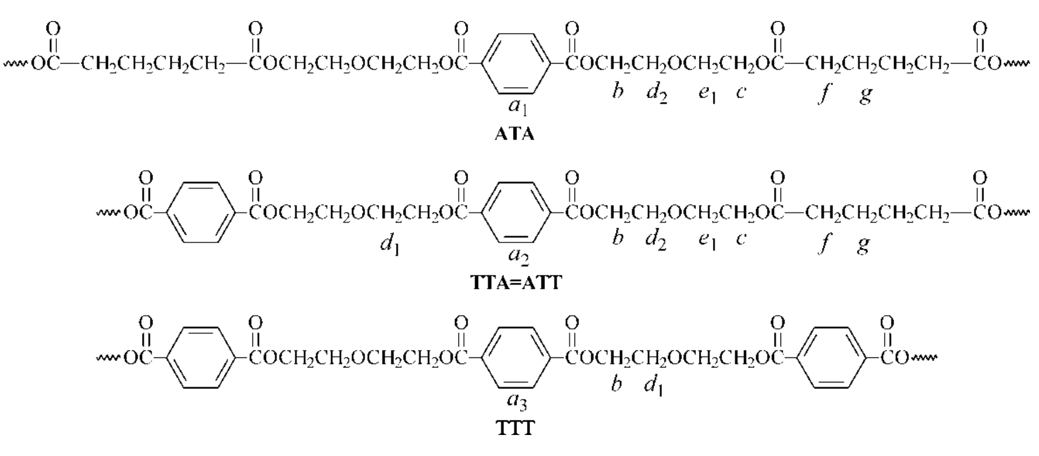

**Fig. 8.** Terephthalate-centered pentad sequences identifying those methylene protons with connectivity to the central aromatic protons as determined by NOESY pulse sequence experiments.

**Table 3.** Structural characteristics of homo- and copolyesters

| Copolyester | $X_T{}^a$ | $B^b$ |
|---|---|---|
| PEOETA-50 | 52 | 1.01 |
| PEOETA-25 | 35 | 0.97 |
| PEOETA-75 | 78 | 0.95 |

[a] Mole fraction of terephthalate units in copolymer ($^1$H NMR).
[b] Degree of randomness ($^1$H-NMR).

The probability of finding an adipate unit next to a terephthalate unit can be calculated using Equation (4).

$$P_{\mathrm{AT}} = \frac{A_{\mathrm{AT}}}{A_{\mathrm{AT}} + A_{\mathrm{AA}}} \tag{4}$$

Using the results obtained from Equations (3) and (4) the degree of randomness ($B$)can be described by (9, 10),

$$B = P_{\mathrm{TA}} + P_{\mathrm{AT}} \tag{5}$$

where $B$ equals 1 for random copolymers, 2 for alternating copolymers, and 0 for block copolymers. The results for the degree of randomness are summarized in Table 3. The copolyesters have an average value of 0.98 indicating that the sequence distribution is random. This is further confirmed by the presence of a single, sharp glass transition in the differential scanning calorimetry (DSC) thermogram (Figure 10). A sample with nonrandom composition distribution would be expected to show a broad transition or possibly multiple transitions corresponding to each segment present.

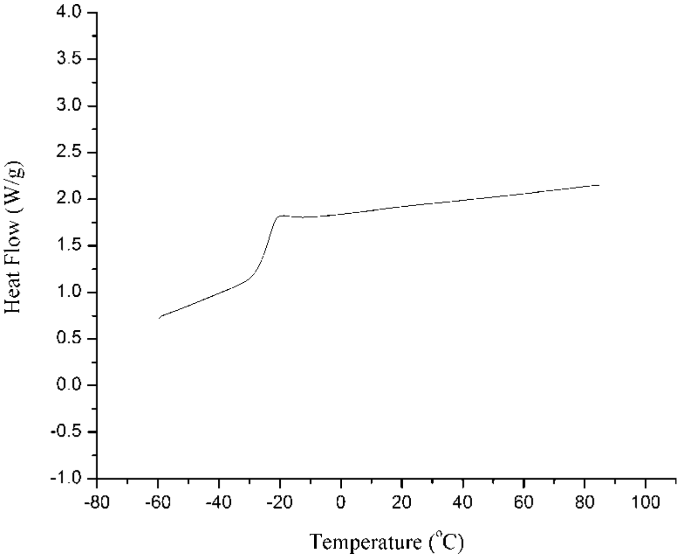

**Fig. 10.** DSC transition curve (second heating) for PEOETA-50.

## 4 Conclusions

Splitting of the terephthalate protons $a$ into a triplet is due to through-space interactions with principally the $b$ and $d$ protons and secondarily the $e_1$, $f$, and $g$ protons of adjacent EOE and A units. Comonomer sequence distribution and chemical shift assignments were determined for PEOETA copolyesters of varying diacid composition using 500 MHz $^1$H-NMR spectroscopy. An average value of 0.98 was found for the degree of randomness of the copolyesters, indicating that the sequence distribution is nearly completely random, which is typical of polyesterification.

## 5 Acknowledgements

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