

SYNTHESIS AND AVERAGE SEQUENCE LENGTH DETERMINATION OF AROMATIC-ALIPHATIC COPOLYESTERS CONTAINING POLY(ALKYLENE OXALATE) UNITS*

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Abstract Two series of aromatic-aliphatic random copolyesters (PEBTOXS) with diverse diol ratios have been synthesized by direct melting polycondensation. Two kinds of diols (glycol (EG) and 1,4-butanediol (BD)) are used in combination in order to adjust crystallization and tensile properties, and three kinds of diacids (dimethyl terephthalate (DMT), diethyl oxalate (DEOX), and sebacic acid (SA)) are involved. ¹H-NMR spectra quantify both composition and structure, and show that the final contents in copolyesters appropriate to the feed ratio. Average sequence lengths of six polyester units are calculated based on the analyses of ¹H-NMR spectra and copolyester structure. The results reveal that the average sequence lengths of sebacate related units increase with the increasing content of sebacic acid in copolyesters, while those of oxalate related units show a slight rise. Decreases of average sequence length are found for all terephthalate units, which may be because of the restriction of rigid aromatic units in reactions.

Keywords: Poly(alkylene oxalate); Copolyester; Synthesis; Average sequence length.

INTRODUCTION

Aliphatic polyesters are of great importance because of their degradability and have drawn much attention^[1, 2]. But the drawbacks in thermal and mechanical properties limit their further applications. Copolymerization^[3–6] and blend^[7, 8] with aromatic polyesters are better choices to modify properties of aliphatic polyesters in both mechanical and thermal aspects. In the mean while, degradability is also expected because some studies have revealed that aromatic polyesters are degradable when they are copolymerized with aliphatic polyesters^[9].

Oxalic acid is the simplest diacid, and poly(alkylene oxalate) possesses relatively higher melting temperature, but there is only a few references addressed the synthesis of copolyesters involving poly(alkylene oxalate)^[10, 11]. Xu and co-workers^[12, 13] have developed preparation of diethyl oxalate (DEOX) by means of coupling with carbon monoxide (CO) as a starting material, which provides a good reason for synthesis of degradable copolyesters containing poly(alkylene oxalate) units. This synthetic route reflects the progress in green chemical technology as well as changes in the polymer landscape.

We have reported the syntheses of random copolyesters poly(ethylene terephthalate-co-oxalate-co-sebacate) (PETOXS) employing diethylene oxalate (DEOX) as one of starting materials^[14]. Poly(ethylene terephthalate) (PET) and poly(ethylene sebacate) (PES) units were used in order to obtain reliable materials for potential application. Thermal stability, degradation rate and mechanical properties are adjusted by the variation of aromatic polyesters content and aliphatic polyester ratios. The characteristic data of DSC barely showed

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endothermic peaks in samples with 60% aromatic polyester units (PET) by molar ratio, indicating that copolyesters with higher fraction of incorporated aliphatic polyester units cannot crystallize at the scanning rate. Moreover, some of the samples were sticky, and the measurements of tensile properties were done only for those with more rigid unit of both terephthalate and oxalate.

We report here the synthesis of random copolyesters (PEBTOXS) involving diethyl oxalate, controlling not only the diacid part (dimethyl terephthalate (DMT), diethyl oxalate (DEOX), and sebacic acid (SA)) but also the diol part (glycol (EG) and 1,4-butanediol (BD)). 1,4-Butanediol is used in combination in diol part, and modified crystallization and tensile properties are expected. The random copolyesters (PEBTOXS) comprising of six polyester units, namely, poly(ethylene terephthalate) (PET), poly(ethylene oxalate) (PEOX), poly(ethylene sebacate) (PES), poly(butylene terephthalate) (PBT), poly(butylene oxalate) (PBOX), and poly(butylene sebacate) (PBS) are prepared by direct polycondensation method under vacuum condition.

Average sequence length is known as an important factor for copolyesters in the understanding of their chemical structure as well as properties. Yamadera and Murano gave a typical reference to evaluate sequence distribution between aromatic polyester and aliphatic copolyesters^[15]. Detailed descriptions of the transesterification between polycarbonate (PC) and polyesters were reported by Ma^[16] and Devaux^[17], respectively. With respect to polyesters from diacids and diols, Kricheldorf^[18] examined the sequence by ¹³C-NMR analysis. Wang *et al.*^[4] investigated the average sequence length of poly(butylene succinate-*co*-ethylene succinate-*co*-ethylene terephthalate). Study on determination of average sequence length for aromatic-aliphatic copolyesters containing 6 polyester units has not been published before.

¹H-NMR spectra are used in this work for testing composition of both diacids and diols in copolyesters. Further investigation on average sequence length on PEBTOXS is undertaken by detailed analysis of chemical structure and proton assignments, and average sequence lengths of six polyester units are also determined.

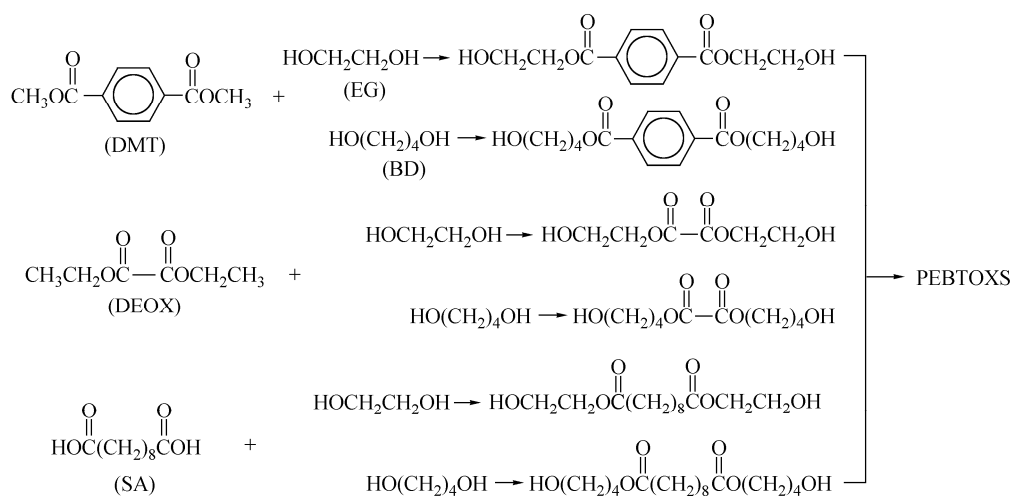
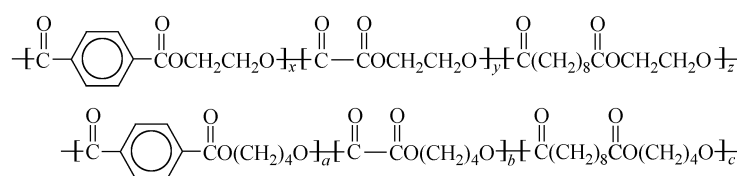
EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) and glycol (EG) were kindly supplied by Chemical Petrol Co., China. Diethyl oxalate (DEOX) and sebacic acid (SA) were all the products of Zhonghe Chemical Plant, Tianjin, China. 1,4-Butanediol (BD) and catalysts were all reagent grades and used as received.

Synthesis

Random copolyesters were synthesized by direct melting polycondensation. First, transesterification of DMT and DEOX with EG and BD were conducted, yielding bis(hydroxyethyl) terephthalate (BHET) and bis(hydroxyethyl) oxalate (BHEOX), bis(hydroxybutyl) terephthalate (BHBT) and bis(hydroxybutyl) oxalate (BHBOX), respectively. EG and BD are also involved in esterification with SA to synthesize bis(hydroxyethyl) sebacate (BHES) and bis(hydroxybutyl) sebacate (BHBS). Secondly, above obtained materials weighed according to molar ratio are added to a four-neck flask equipped with a mechanically sealed stirrer and condenser. Melting polycondensation was proceeded at $(255 \pm 2)^{\circ}\text{C}$ for 150 min with Ti derivative as a catalyst under nitrogen atmosphere and vacuum condition less than 133 Pa. The synthetic route and chemical structure of copolyester PEBTOXS are given in Scheme 1 and Scheme 2, respectively.

**Scheme 1** Synthetic route of PEBTOXS**Scheme 2** Chemical structure of PEBTOXS**Measurements**

Intrinsic viscosity of copolyester was determined by an Ubbelohde viscometer in a thermostat at $(25.0 \pm 0.1)^\circ\text{C}$ using phenol/1,1,2,2-tetrachloroethane (50/50, *W/W*) as solvent.

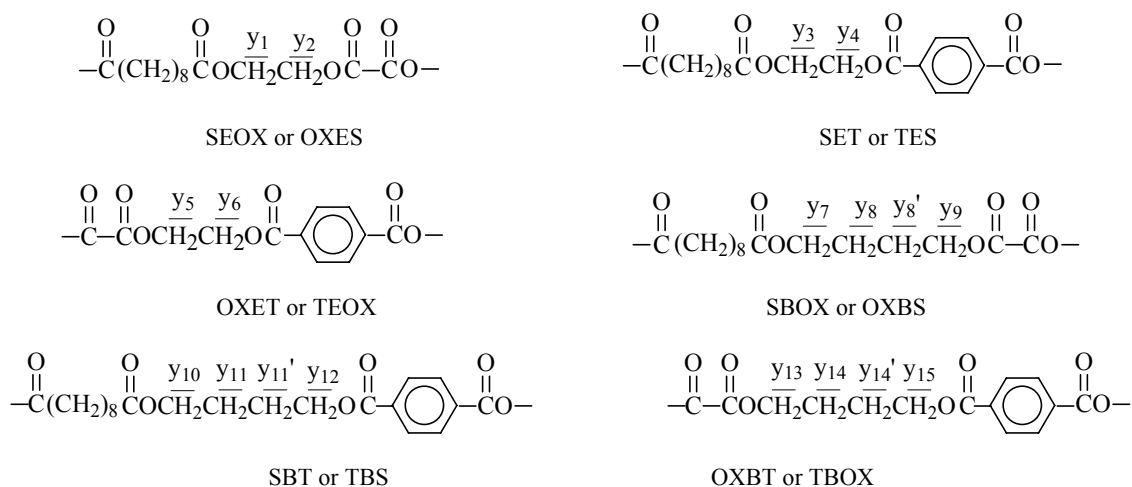
The chloroform solved copolyester samples were precipitated in a large excess of anhydrous methanol. The precipitated polymers were dried overnight in *vacuo* at environmental temperature. ^1H -NMR spectra of copolyesters samples were recorded in deuterated chloroform (CDCl_3) with tetramethylsilane as internal standard on a Varian Inovia 500 MHz spectrometer.

RESULTS AND DISCUSSION**Synthesis**

Random copolyesters PEBTOXS appear opaque-transparent as well as hard-soft semi-crystalline solids at room temperature based to compositions. The samples with varying feed ratios are given in Table 1, in which values of intrinsic viscosity are also reported.

Table 1. Designated samples of copolyesters

Sample	Feed ratio (mol%)			$[\eta]$ (dL/g)
	EG/(EG+BD)	OX/(OX+S)	T/OX/S	
T40E60-100	60	100	40/60/0	0.7109
T40E60-80	60	80	40/48/12	0.7458
T40E60-60	60	60	40/36/24	0.7538
T40E40-100	40	100	40/60/0	0.7721
T40E40-80	40	80	40/48/12	0.8792
T40E40-60	40	60	40/36/24	0.8245



b) Assignments of protons for probable hetero-linkages

Scheme 3 Assignments of protons for PEBTOXS

Moreover, there are 12 probable dyads in PEBTOXS, namely, SES, OXEOX, TET, SBS, OXBOX, TBT, SEOX, SET, OXET, SBOX, SBT, and OXBT. The structures for homo- and hetero-linkages dyads and proton assignments are delineated in Schemes 3(a) and 3(b), respectively.

The absorbances of protons in glycol residues (x_1 – x_3 and y_1 – y_6) are a set of peaks from $\delta = 4.261$ to 4.698 , and the protons of tetramethylene in BD (x_5 , x_7 , x_9 , y_7 , y_9 , y_{10} , y_{12} , y_{13} , and y_{15}) are also included in this range. Other protons in tetramethylene units (x_4 , x_6 , x_8 , y_8 , y_8' , y_{11} , y_{11}' , y_{14} , y_{14}') appear as a set of profiles at about $\delta = 1.693$ to 1.965 .

The composition of BD in copolyester can be determined by proton integration intensity in the range of $\delta = 1.693$ to 1.965 . The content of EG is obtained from the integration intensity from $\delta = 4.261$ to 4.698 by subtracting the reiteration of BD in this range. The content of EG and BD as well as their ratios are illustrated in Fig. 2 for comparison. The percentages of EG in diols (EG/(EG+BD)) are ranging from 59.1 mol% to 68.8 mol% and 35.5 mol% to 44.2 mol% in EG-rich and BD-rich series, respectively, which agrees well with the feed ratio.

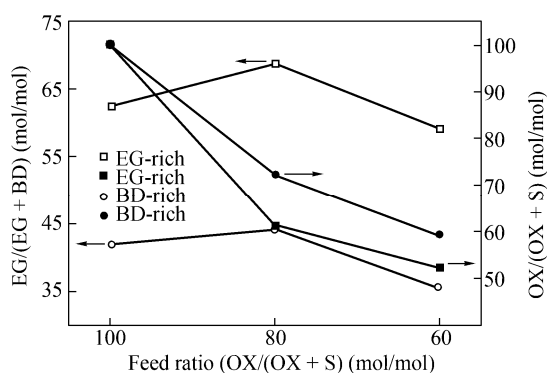


Fig. 2 Comparison of feed ratios with compositions in copolyesters

A special problem is that there is no proton in oxalic acid residue in $^1\text{H-NMR}$ spectra. But the analyses of the resonances in $^1\text{H-NMR}$ spectra strongly suggest the proposed 12 dyads and demonstrate the existence of oxalate units in PEBTOXS copolyesters, which will be discussed in detail in the structure section. If all the diols

participated in copolymerization are linked with the diacids, the mole value of oxalate can be achieved on basis of the intensity of diols detected by $^1\text{H-NMR}$. To obtain the reliable mole value of oxalate units in copolyesters, we detract the molar values of both terephthalate (determined by the integration intensity at $\delta = 8.100$) and sebacate (derived from integration intensity of protons s_3 at $\delta = 2.316$) from the sum of diols (EG+BD), and the results are also included in Fig. 2. The molar ratios of oxalate and sebacate (OX/(OX+S)) also confirm the consistency of feed ratio and composition.

Structure

Properly comparing of structure and sequence length requires reasonable analyses by referring to related literatures^[20, 21]. Protons in Scheme 3 can be divided into groups according to the probable diester environment and chemical shift, and the assignments of proton signals are illustrated in Fig. 3.

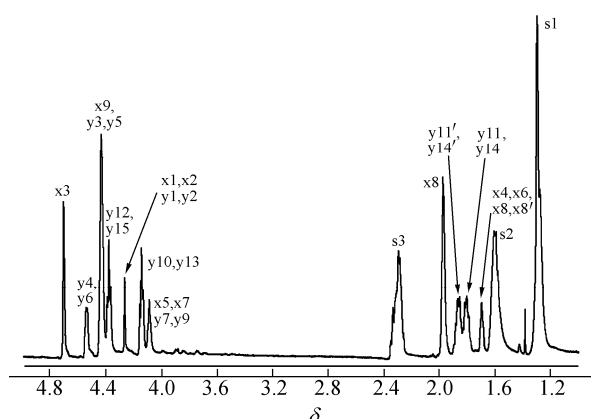


Fig. 3 Magnified part of $^1\text{H-NMR}$ spectrum for T40E40-60

In detail, protons in glycol and 1,4-butanediol residues with terephthalic attached in both sides appear at $\delta = 4.698$ (TET, x_3) and $\delta = 4.427$ (TBT, x_9), respectively. Signals at $\delta = 4.533$ (y_6 and y_4) and $\delta = 4.427$ (y_3 and y_5) are the protons in glycol residue for hetero-linkage of aromatic and aliphatic diacid (SET or TES, and SEOX or OXES). Aromatic and aliphatic diacid hetero-linkages of protons in BD are sited at $\delta = 4.376$ (y_{12} and y_{15}) and $\delta = 4.139$ (y_{10} and y_{13}) (SBT or TBS, and SBOX or OXBS), respectively. Included at $\delta = 4.261$ (x_1 , y_1 , y_2 , and x_2) (SES, SEOX or OXES, and OXEOX) and $\delta = 4.086$ (x_5 , y_7 , y_9 , and x_7) (SBS, SBOX or OXBS, and OXBOX) are the resonances of glycol and 1,4-butanediol residue related aliphatic-aliphatic linkages, respectively. Other protons in tetramethylene (x_8 , y_8 , $y_{8'}$, y_{11} , $y_{11'}$, y_{14} , $y_{14'}$, x_6 , and x_4) showing signals at $\delta = 1.965$ to 1.693 have also been assigned in Fig. 3. The assignments of protons with chemical shift are summarized in Table 2.

Table 2. Assignments of proton signals

Symbol	Protons and chemical shift δ							
	Proton	δ	Proton	δ	Proton	δ	Proton	δ
SES	x_1	4.261						
OXEOX	x_2	4.261						
TET	x_3	4.698						
SBS	x_5	4.086	x_4	1.693				
OXBOX	x_7	4.086	x_6	1.693				
TBT	x_9	4.427	x_8	1.965				
SEOX or OXES	y_2	4.261	y_1	4.261				
SET or TES	y_4	4.533	y_3	4.427				
OXET or TEOX	y_6	4.533	y_5	4.427				
SBOX or OXBS	y_9	4.086	y_7	4.086	$y_{8'}$	1.693	y_8	1.693
SBT or TBS	y_{12}	4.376	y_{10}	4.139	$y_{11'}$	1.863	y_{11}	1.797
OXBT or TBOX	y_{15}	4.376	y_{13}	4.139	$y_{14'}$	1.863	y_{14}	1.797

With the analyses of chemical structure and dyads in Scheme 3 and Fig. 3, the intensities of protons have the relationships as follow:

$$I_{x_4} = I_{x_5}, I_{x_6} = I_{x_7}, I_{x_8} = I_{x_9}$$

$$I_{y_1} = I_{y_2}, I_{y_3} = I_{y_4}, I_{y_5} = I_{y_6}$$

$$I_{y_7} = I_{y_8} = I_{y_9} = I_{y_{10}}, I_{y_{11}} = I_{y_{12}}, \text{ and } I_{y_{13}} = I_{y_{14}} = I_{y_{15}}$$

in which I refers to the integration area of protons in $^1\text{H-NMR}$ spectra, and the subscripts represent the corresponding designated protons in Scheme 3.

The peaks at $\delta = 4.376$ (y_{12} and y_{15}) and $\delta = 4.139$ (y_{10} and y_{13}) have almost identical intensity, coupled with the analysis of related chemical environment of protons, the integration area of y_{12} , y_{15} , y_{10} , and y_{13} can be obtained. The same manipulation is also applied to the intensity of protons from y_3 to y_6 . The intensity in proton groups of x_1 , y_1 , y_2 , and x_2 as well as that in proton groups of x_5 , y_7 , y_9 , and x_7 is distributed according to the ratio of oxalate and sebacate (OX/(OX+S)) in copolyesters. The results of relative intensity for protons are collected in Table 3.

Table 3. Relative intensity of protons

Sample	Intensity											
	x_1	x_2	x_3	x_4	x_6	x_8	y_1 (y_2)	y_3 (y_4)	y_5 (y_6)	y_7 (y_9)	y_{10} (y_{12})	y_{13} (y_{15})
T40E60-100	—	—	14.98	—	—	2.70	—	1.95	1.95	—	0.19	0.19
T40E60-80	0.47	0.64	15.02	0.10	0.14	7.88	0.28	3.57	3.57	0.12	1.23	1.23
T40E60-60	2.47	2.40	14.96	1.24	1.21	12.79	1.22	5.96	5.96	1.22	4.07	4.07
T40E40-100	—	—	14.93	—	—	20.19	—	1.33	1.33	—	0.86	0.86
T40E40-80	0.18	0.46	14.97	0.19	0.48	25.95	0.16	3.11	3.11	0.33	2.99	2.99
T40E40-60	1.92	2.79	15.06	3.02	4.39	39.69	1.18	4.48	4.48	3.71	9.76	9.76

Table 3 shows that for the EG-rich series the intensities of protons in all EG-related dyads (OXEOX, SEOX, SET, and OXET) are larger than those of BG-related dyads (OXBOX, SBOX, SBT, and OXBT) on regular basis. Whereas, BG-related protons show relatively larger intensities than those of EG-related ones, when the contents of BG are overweight in BG-rich series samples. The results of intensity confirm the composition of PEBTOXS copolyesters obtained above.

Average Sequence Length

Yamadera's manipulation^[15] is often adopted to calculate the average sequence length in copolyesters. We performed mathematical calculations on basis of Yamadera's equations and Wang's work^[4] to obtain the average sequence length ($\bar{L}$) of six polyester units in PEBTOXS. The ultimate expressions are as follows:

$$\bar{L}_{\text{PES}} = \frac{I_{x_1} + (I_{y_1} + I_{y_3})/2}{(I_{y_1} + I_{y_3})/2} \quad (1)$$

$$\bar{L}_{\text{PBS}} = \frac{I_{x_4} + (I_{y_7} + I_{y_{10}})/2}{(I_{y_7} + I_{y_{10}})/2} \quad (2)$$

$$\bar{L}_{\text{PEOX}} = \frac{I_{x_2} + (I_{y_2} + I_{y_5})/2}{(I_{y_2} + I_{y_5})/2} \quad (3)$$

$$\bar{L}_{\text{PBOX}} = \frac{I_{x_6} + (I_{y_9} + I_{y_{13}})/2}{(I_{y_9} + I_{y_{13}})/2} \quad (4)$$

$$\bar{L}_{\text{PET}} = \frac{I_{x_3} + (I_{y_4} + I_{y_6})/2}{(I_{y_4} + I_{y_6})/2} \quad (5)$$

$$\bar{L}_{\text{PBT}} = \frac{I_{x_8} + (I_{y_{12}} + I_{y_{15}})/2}{(I_{y_{12}} + I_{y_{15}})/2} \quad (6)$$

The calculated average sequence lengths for six polyester units in PEBTOXS are illustrated in Fig. 4.

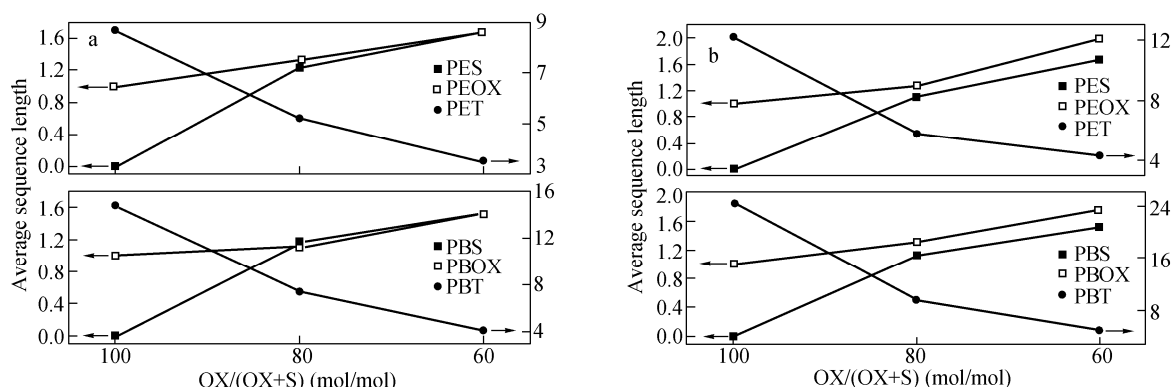


Fig. 4 Variation of average sequence length of copolyesters: (a) EG-rich copolyesters and (b) BD-rich copolyesters

As the contents of sebacate increase, the average sequence lengths of sebacate-related units (PES and PBS) increase, whereas the average sequence lengths of both PET and PBT units decrease remarkably. Moreover, there is a slight rise of oxalate related polyester units (PEOX PBOX) when the content of sebacate rises, which could be explained by the flexibility difference between aliphatic and aromatic units leading to the different ability during the reaction^[4]. The addition of flexible sebacate units favors the copolymerization with aliphatic units, while the involvement of aromatic units in copolymerization is hindered by its rigidity.

CONCLUSIONS

Copolyesters of PEBTOXS containing six polyester units with diethyl oxalate as one of starting materials have been successfully synthesized by direct melting polycondensation. The values of intrinsic viscosity are in the range of 0.7109–0.8792 dL/g.

¹H-NMR spectra corroborate copolyesters structure, and the analyses as well as calculation reveal that compositions of copolyesters agree well with feed ratios. Quantitative determination of average sequence lengths for polyester units is done with the equations proposed by Yamadera. An increase in average sequence length with increasing content of sebacate units is found for both PES and PBS units in copolyesters, while those of all terephthalate units decrease drastically.

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