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SYNTHESIS AND PROPERTIES OF HYDROPHILIC POLYMERS. 4. PREPARATION AND CHARACTERIZATION OF POLY(OXYETHYLENE) TELECHELICS WITH DIFFERENT AROMATIC TERMINI

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ABSTRACT

Several telechelic compounds were prepared by terminal functionalization of poly(oxyethylene) diacid via the reaction of the carboxylic groups with different aromatic amines. Starting from the telechelic diacid, the corresponding diacid chloride was prepared with thionyl chloride after which the compound was allowed to react with aniline, 2-naphtylamine, and 2-aminoanthracene. The telechelic products were characterized by UV/Vis, ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy. The UV/Vis spectrometric data were compared to those of the corresponding amines. In addition, refractive indices and solubility characteristics were also determined. In addition, the spectroscopic data were compared with respect to increasing terminal chain extension by the three aromatic compounds.

INTRODUCTION

Telechelic compounds have found considerable interest as versatile intermediates in many fields [1]. Among those, poly(oxyethylene)-based telechelic compounds are dominant for many applications due to their salient properties such as their strong solublizing power in many solvents [2-4]. They have been used for peptide synthesis [4], enzyme modification [5], and for the development of drug derivatives [6-8]. Recently, they have also been employed as building blocks for dendrimers [9].

Many of these applications require certain end-groups, and telechelic modification is therefore an important prerequisite for the practical use of such basis telechelics as poly(ethylene glycol). Consequently, a number of functionalization reactions have been proposed and investigated [3, 8, 10-13].

Telechelic derivatives of poly(oxyethylene) with terminal para-substituted phenyl ether moieties, e.g., α,ω-di(4-formylphenyloxy) poly(oxyethylene), have been described [14]. Here we report on the synthesis and properties of telechelic poly(oxyethylene) dervatives with three different unsubstituted aromatic terminal groups.

EXPERIMENTAL

Materials

Toluene, diethylether, hexane, chloroform, dichloromethane, and pyridine were purified and dried according to the literature [15,16]. Thionyl chloride (from Merck) was purified by refluxing a mixture of 10 wt% linseed oil in thionylchloride for 2 hours and subsequent distillation. Aniline was distilled and 2-naphthylamine (both from Fluka) was recrystallized prior to use. 2-Aminoanthracene was prepared via the reduction of 2-aminoanthrachinone [17] and purified by recrystallization from ethanol (mp 238-240°C).

Poly(ethylene glycol) 600 diacid (acid number 175, 96-98%, from Fluka) (POE-A) was dried over Na_2SO_4.

Elemental analysis (calcd for $n = 12$): $C_{28}H_{54}O_{17}$ (662.74). calcd: C 50.75, H 8.21; Found: C 50.28, H 9.05. $n = 11.93$ (calcd from ^{1}H-NMR data).

The physicochemical properties of POE-A are listed in Table 1 and 2 and the spectroscopical data in Table 3.

Instruments and Methods

NMR: Bruker AC 250 (^{1}H: 250 MHz; ^{13}C: 62.9 MHz), Bruker ARX 250 (^{1}H: 250 MHz; ^{13}C: 62.9 MHz). The degree of polymerization values were calculated from the ratio of methylene protons of the oxyethylene unit and the methylene protons vicinal to the carbonyl group. UV/Vis: Perkin-Elmer Lambda 5 Spektrophotometer, Otsuka MCPD 1000. IR: Perkin-Elmer 1310 Infrared Spectrophotometer. Elemental analysis: Carlo Erba Elemental Analyzer 1106. Viscosimetry: Ubbelohde viscometer with a suspended level bulb ($K = 0.01$, Schott). pH measurements: Metrohm pH-meter E 512. TLC chromatography: Butanone saturated with water (1:1, v:v, butanone:water) as the elution solvent. The TLC was performed with silica gel plates 60 F_{254} (0.2 mm, 20·20, Merck), and the Dragendorff-Bürger reagent was used for detection [18].

α,ω-Di(chlorocarbonylmethylene) Poly(Oxyethylene) (POE-Cl)

Two grams of dry poly(ethylene glycol) 600 diacid (POE-A) (6.24 mmol carboxylic acid groups) was placed in a 10-mL round-bottom flask equipped with a reflux condenser, dropping funnel, and magnetic stirrer. Then 5 mL thionyl chloride (68.9 mmol) was added dropwise at 0°C (30 minutes). The temperature was slowly raised to room temperature over 1 hour and finally kept at 70°C for 6 hours. It is advisable to place a calcium chloride tube, an empty trap, and a trap with a 2-N NaOH solution on the top of the condenser to exclude moisture and absorption of HCl and SO_2. Then the excess of thionyl chloride was distilled off under vacuum at 40°C. Then 10 mL dichloromethane or toluene was added to the solution, and the solvents were evaporated under vacuum to remove traces of thionyl chloride. Yield: 2.1 g (100%).

Elemental analysis (calcd for $n = 12$): $C_{28}H_{52}Cl_2O_{15}$ (699.62). Calcd: C47.00, H 7.32, Cl 9.91; Found: C 47.79, H 7.68, Cl 10.03. $n = 12.00$ (calcd from ^{1}H-NMR data).

IR (film): ν (cm^{-1}) = 2820(s), 1780(s), 1440(m), 1340(m), 1280(m), 1240(m), 1100(s), 920(s), 840(m), 740(s).

^{1}H NMR ($CDCl_3$): δ (ppm) = 4.42 (s, $-CO-CH_2-O-$), 3.71-3.54 (m, $O-CH_2-CH_2-O$).

^{13}C NMR ($CDCl_3$): δ (ppm) = 171.9 ($-CO-CH_2-O-$), 74.9, 71.5, 71.2, 71.1, 70.5, 68.5, 17.2.

α,ω-Di(phenylamidomethylene) Poly(Oxyethylene) (1) and α,ω-Di(2-naphthylamidomethylene) Poly(Oxyethylene) (2)

A solution of aniline (624 μL, 6.84 mmol, for **1**) or 2-naphthylamine (0.98 g, 6.84 mmol, for **2**) and pyridine (1.0 mL, 12.38 mmol) in 50 mL toluene was placed in a 100-mL round-bottom flask equipped with a dropping funnel and magnetic stirrer. Then POE-Cl (2.1 g, 6.24 mmol acyl chloride groups) was added to the amine solution at room temperature under vigorous stirring. After 2 hours the solution was filtered off and treated in a separatory funnel with 10 mL HCl (1 N) to remove any excess amine and pyridine. The organic layer was washed 2–3 times with water and dried over Na_2SO_4. After filtering off and evaporating the solvent, the oil was treated with 25 mL *n*-hexane at 0°C, washed 2–3 times with 10 mL *n*-hexane, and finally dried under vacuum. For enhanced purification, the oil was redissolved in toluene or chloroform and then poured again into *n*-hexane and dried under vacuum.

Compound 1

Yield: 0.9 g (37%)

Elemental analysis (calcd for $n = 12$): $C_{40}H_{64}N_2O_{15}$ (812.97). Calcd: C 59.10, H 7.93, N 3.45; Found: C 59.28, H 8.03, N 4.27. $n = 12.00$ (calcd from ^{1}H-NMR data).

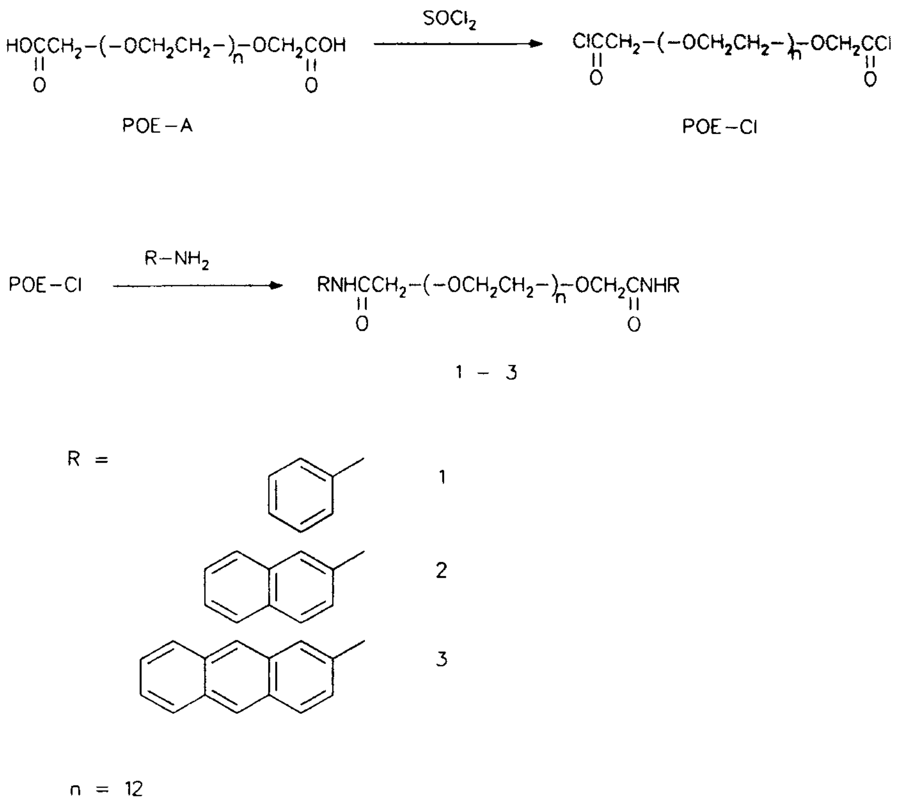


FIG. 1. Reaction scheme for the terminal functionalization of poly(oxyethylene).

TABLE 1. Physicochemical Data of the Telechelic Compounds Based on Poly-(Oxyethylene)

	POE-A	POE-Cl	**1**	**2**	**3**
State of matter	Oil	Oil	Oil	Oil	Solid
Color	Light yellow	Yellow-orange	Brown-red	Brown-red	Light brown
mp in °C	−30/−25	—	—	−25/−20	103-108
n_D^{20}	1.467	1.474	1.509	1.557	—
[η] in mPa·s[a]	5.1	—	6.4	6.7	5.6
Yield in %	—	100	37	40	36

[a] Chloroform as solvent.

TABLE 2. Solubility of Telechelic Compounds in Different Solvents[a]

Solvent	POE-A	1	2	3
Water	+	#	–	–
Methanol	+	+	+	#
Acetone	#	+	+	+
Dichloromethane	+	+	+	+
Chloroform	+	+	+	+
Diethylether	–	+	+	#
Toluene	#	+	+	+
n-Hexane	–	–	–	–

[a] + = soluble, # = slightly soluble, – = insoluble.

UV/Vis (menthanol): λ_{max} = 243.52 nm.

IR (film): ν (cm^{-1}) = 3490(m), 3310(m, N—H), 3060(w), 2860(s), 1670(s, C=O), 1600(m), 1530(s), 1500(w), 1440(s), 1300(m), 1100(s C—O—C), 950(m), 840(w), 750(m), 690(m).

^{1}H NMR ($CHCl_3$): δ (ppm) = 8.79 (s, 1H, N—H), 7.59 (dd, J = 8 Hz and J = 1 Hz, 2H phenyl), 7.30 (t, J = 8 Hz, 2H, phenyl), 7.08 (t, J = 7 Hz, 1H, phenyl), 4.09 (s, 2H), 3.75-3.54 (m, 4H), 2.35-2.15 (m, $O—CH_2—CH_2$).

^{13}C NMR ($CHCl_3$): δ (ppm) = 168.2 (C=O), 137.49, 128.89, 124.36, 120.07 (phenyl), 74.50 ($—NH—CO—CH_2—O$), 71.23, 70.84, 70.72, 70.56, 70.47, 70.17 ($O—CH_2—CH_2—O$), 68.50 ($O—CH_2—$).

Compound 2

Yield: 1.1 g (40%)

Elemental analysis (calcd for n = 12): $C_{48}H_{68}N_2O_{15}$ (913.09). Calcd: C 63.14, H 7.51, N 3.07; Found: C 63.69, H 7.82, N 3.44. n = 12.21 (calcd from ^{1}H NMR data).

TABLE 3. NMR Spectroscopic Data of the Telechelic Compounds Investigated (in chloroform)

	POE-A	POE-Cl	1	2	3
^{1}H NMR, δ in ppm					
—NH or —OH	6.75	–	8.79	8.95	9.01
$—O—CH_2—CO—$	4.03	4.42	4.09	4.14	4.17
^{13}C NMR, δ in ppm					
—CO—	172.26	171.9	168.2	168.4	168.5
$—O—CH_2—CO—$	74.9	75.0	75.1	75.0	75.1

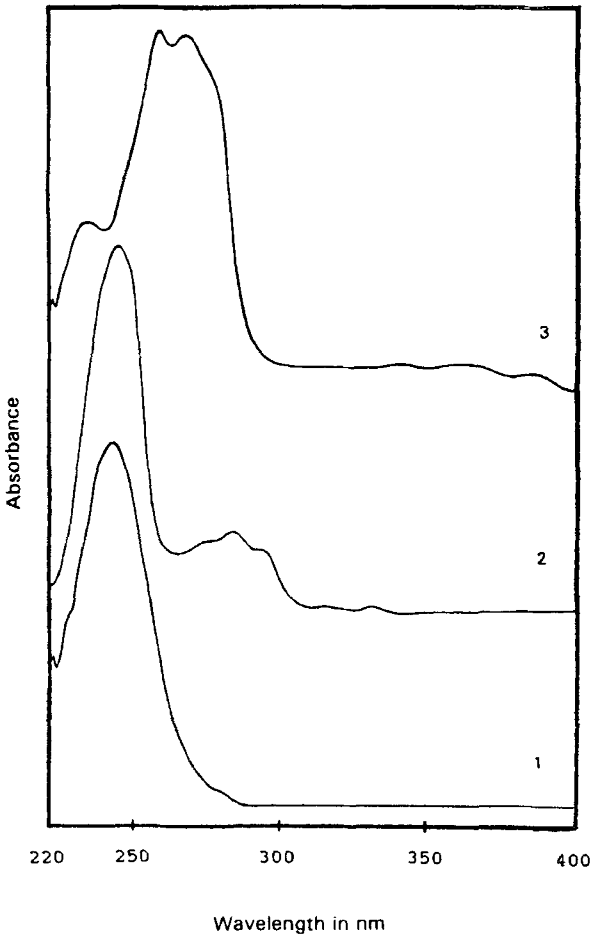


FIG. 2. UV/Vis spectra of telechelic compounds **1**, **2**, and **3** in methanol.

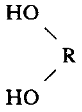
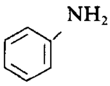
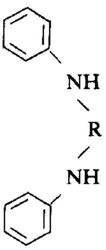
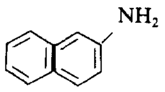
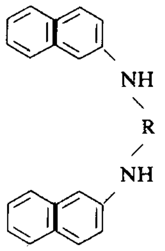
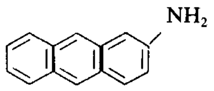
UV/Vis (methanol): λ_{max} (nm) = 243.52, 282.60, 313.59, 329.19.

IR (film): ν (cm^{-1}) = 3450(w) 3300(m, N—H), 3050(w), 2860(s), 1680(s, C=O), 1540(s), 1500(m), 1440(m), 1350(m), 1280(m), 1240(m), 1100(s, C—O—C), 940(m), 850(m), 750(m).

^1H NMR ($CHCl_3$): δ (ppm) = 8.95 (s, 1H, N—H), 8.66 (s, 1H, naphthyl), 7.72 (q, J = 4.5 Hz, 3H, naphthyl), 7.56 (dd, J = 8.8 Hz, J = 2 Hz, 1H, naphthyl), 7.35 (p, J = 7.5 Hz, 2H, naphthyl), 4.08 (s, 2H, —NHCO—CH_2—O), 3.76–3.43 (m, 4H).

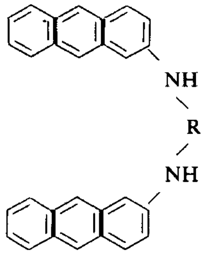
^{13}C NMR ($CHCl_3$): δ (ppm) = 168.41 (C=O), 135.04, 133.84, 130.72, 128.59, 127.65, 127.52, 126.37, 124.93, 120.14, 116.76 (naphthyl), 75.02 (—NHCO—CH_2—O), 72.02, 71.24, 70.80, 70.66, 70.51, 70.40, 70.11, (O—CH_2—CH_2—O), 68.45 (O—CH_2—).

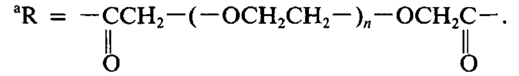
TABLE 4. UV/Vis Spectrometric Data of the Telechelic Polymers Investigated and Their Corresponding Aromatic Amine Analogues (in methanol)[a]

	λ_{max} in nm [ε in $L \cdot mol^{-1} \cdot cm^{-1}$]
	236.78
	238.13, 285.29
	243.52 [37,871.7]
	238.13, 279.90, 339.19
	243.52 [109,585.9], 282.60 [21,422.8], 329.19
	259.69, 335.14, 403.86

(continued)

TABLE 4. Continued

	λ_{max} in nm [ε in L·mol^{-1}·cm^{-1}]
	258.34 [148,126.4], 267.77 [145,505.3], 340.53, 363.44



[a] $R = -\underset{\underset{O}{\|}}{C}CH_2-(-OCH_2CH_2-)_n-OCH_2\underset{\underset{O}{\|}}{C}-.$

α,ω-Di(2-anthranylamidomethylene) Poly(Oxyethylene) (3)

A solution of 2-aminoanthracene (0.13 g, 0.68 mmol) and pyridine (0.5 mL, 6.19 mmol) in 130 mL toluene were placed in a 250-mL round-bottom flask with a dropping funnel and magnetic stirrer. Then POE-Cl (0.21 g, 0.64 mmol acyl chloride groups) was added dropwise at room temperature under vigorous stirring. After 2 hours the yellow colored solution was filtered off and treated in a separatory funnel with 10 mL HCl (1 N) to remove any excess of 2-aminoanthracene and pyridine. The toluene layer was washed 2–3 times with 10 mL water, and the organic phase was separated and dried over Na_2SO_4. After evaporation of toluene the product was obtained in solid form. The light brown solid was washed with 10 mL diethylether (2–3 times) at 0°C and finally dried under vacuum. Yield 0.11 g (36%).

Elemental analysis (calcd for $n = 12$): $C_{56}H_{72}N_2O_{15}$ (1013.21). Calcd: C 66.39, H 7.16, N 2.76; Found: C 67.13, H 6.90, N 3.27. $n = 12.00$ (calcd from ^{1}H-NMR data).

UV/Vis (methanol): λ_{max}(nm) = 232.74, 258.34, 267.77, 340.53, 363.44, 386.35.

IR (film from $CHCl_3$): ν (cm^{-1}) = 3350(w), 3280(m, N—H), 3020(w), 2900(s), 2840(s), 1660(s, C=O), 1530(m), 1500(s), 1440(m), 1330(w), 1290(m), 1230(w), 1100(s, C—O—C), 940(w), 880(m), 740(m).

^{1}H NMR ($CHCl_3$): δ (ppm): 9.00(s, 1H, N—H), 8.49 (s, 1H, anthracyl), 8.34 (d, J = 5.9 Hz, 2H, anthracyl), 7.94 (d, J = 8.5 Hz, 3H, anthracyl), 7.51 (d, J = 9.1 Hz, 1H, anthracyl), 7.45–7.35 (m, 2H, anthracyl), 4.17 (s, $-NHCO-CH_2-O$), 3.77–3.50 (m, $O-CH_2-$).

^{13}C NMR ($CHCl_3$): δ (ppm): 168.51 (C=O), 134.31, 132.18, 131.94, 131.19, 129.36, 129.07, 128.16, 127.94, 126.01, 125.76, 125.53, 125.02, 120.91, 115.92 (anthracyl), 75.05 ($-NHCO-CH_2-O$), 71.30, 70.67, 70.54, 70.17 ($-CH_2-CH_2-O$), 68.47 ($-O-CH_2-$).

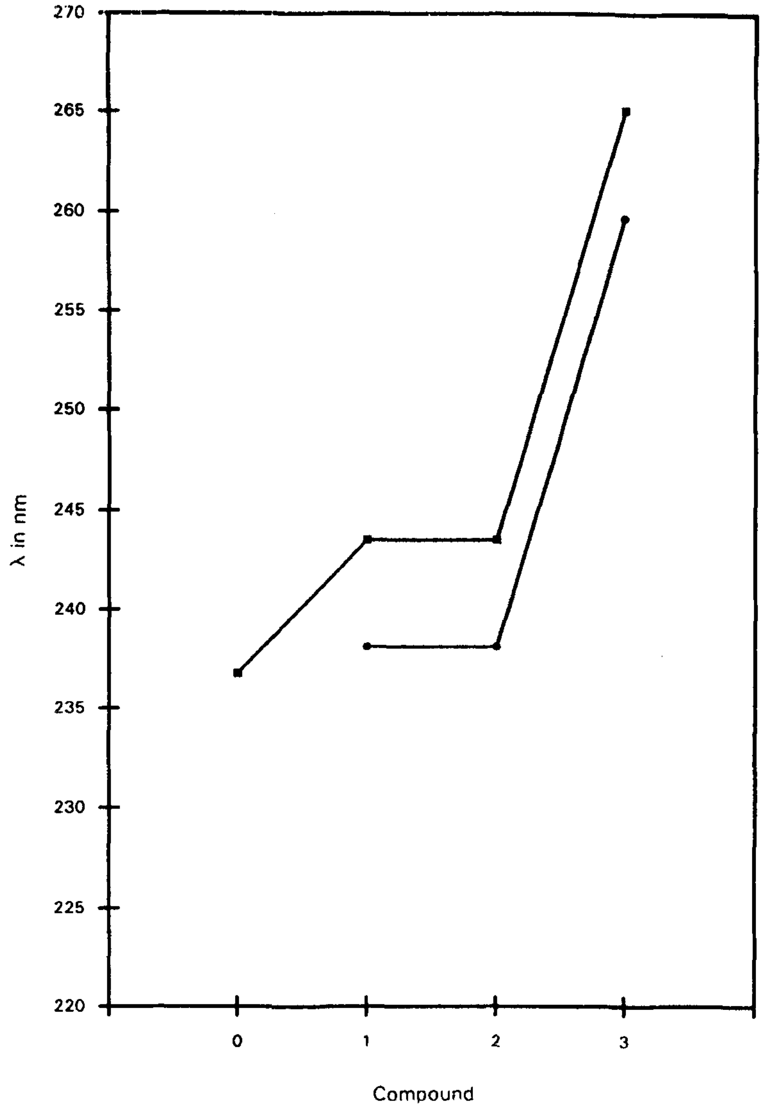


FIG. 3. Graphical representation of λ_{max} values of telechelic compounds POE-A, 1, 2, 3 (■) and their amines (●) as a function of the number of terminal aromatic units.

RESULTS AND DISCUSSION

Three different telechelic compounds based on poly(oxyethylene) with aromatic termini were synthesized starting from α,ω-dicarboxymethylene poly(oxyethylene). The aromatic amines aniline, 2-naphthylamine, and 2-aminoanthracene were reacted with the telechelic poly(oxyethylene) dicarboxylic acid to produce the corre-

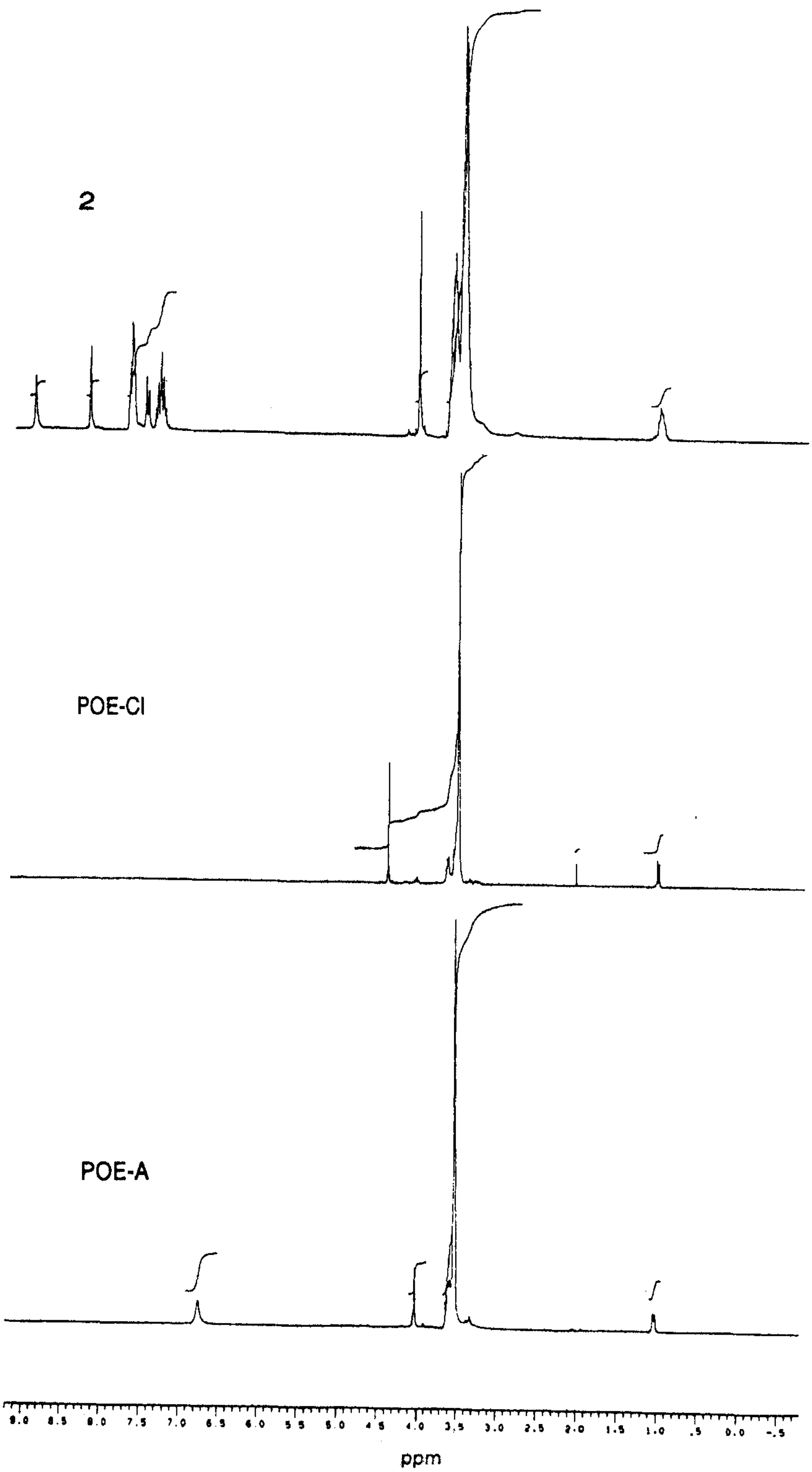


FIG. 4. ¹H-NMR spectra of telechelic compounds POE-A, POE-Cl, and **2**.

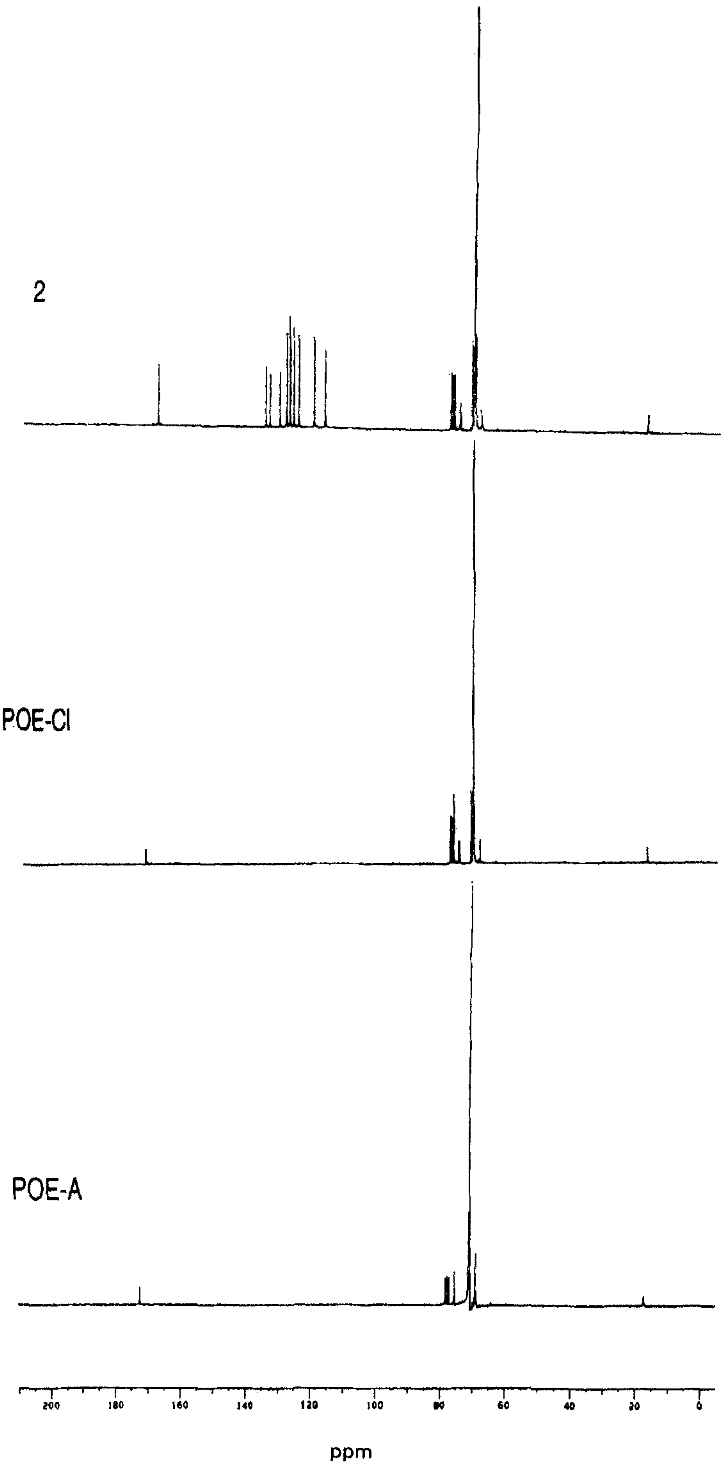


FIG. 5. ^{13}C-NMR spectra of telechelic compounds POE-A, POE-Cl, and **2**.

sponding amide telechelics. The spectroscopic characterization of the telechelics **1–3** indicated quantitative conversion to the corresponding aromatic-terminal telechelics.

The telechelic acid chloride was prepared from the diacid (POE-A) using thionyl chloride without adding a solvent (Fig. 1). The next step, the reaction of the acid chloride with the aromatic amine, was performed in a mixture of pyridine and toluene. All telechelic amides were obtained with yields of about 40% in the pure isolated form. It should be noted in this context that the acid chloride was not very stable and showed a change in color from yellow to dark-brown within 1 day, thus hydrolysis can be assumed. Therefore, direct reaction of the acid chloride is recommended for routine synthesis. In this study, however, the isolation was performed in order to be able to characterize the product.

The physicochemical data of telechelic POE-A, POE-Cl, and **1**, **2**, and **3** are given in Table 1. Table 2 shows the solubility characteristics of the new telechelic polyethers **1**, **2**, and **3** in comparison to the diacid educt. It is evident that the introduction of two or more terminal aromatic rings decreases the solubility in water. On the other hand, the general solubility characteristics of poly(oxyethylene) are not significantly changed in respect to organic solvents.

The NMR and IR spectroscopic data of the telechelics **1**, **2**, **3** and the educts POE-A and POE-Cl are shown in Table 3. Figure 2 shows the UV/Vis spectra and

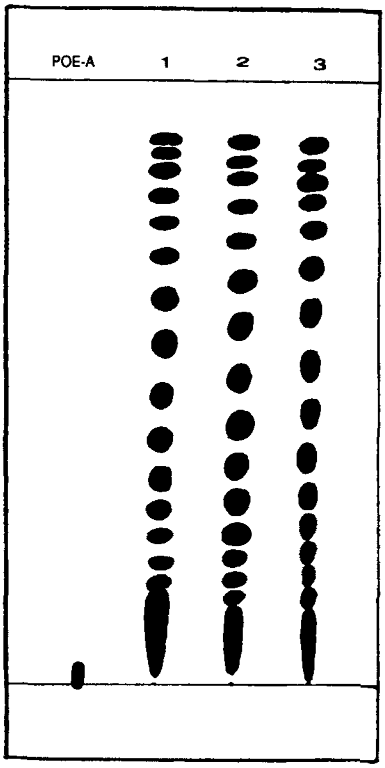


FIG. 6. Thin-layer chromatograms of the telechelic compounds POE-A, **1**, **2**, and **3** (elution solvent: butanone-water (1:1), butanone phase).

the UV/Vis spectroscopic data of the telechelic compounds **1**, **2**, and **3**, and their corresponding low-molecular analogues are compared in Table 4.

Figure 3 shows the shift of the absorption maximum to longer wavelengths during the formation of the aromatic telechelic amide from the corresponding aromatic amine (bathochromic effect). NMR spectra are shown in Figs. 4 and 5. The disappearance of the proton signal after the formation of the chloro derivative of the poly(oxyethylene) diacid and also the shift of the proton signal of the α-methylene group during the preparation of POE-Cl can be seen in Fig. 4.

In addition, the aromatic signal and the proton signal pertaining to the amide are evident for product **2**. The unchanged signal is attributed to the polyether chain. In Fig. 5, obviously two additional distinct signals from the carbons of the aromatic nuclei as well as a shift of the carbon signal of the carboxylic group toward the amide group can be discerned.

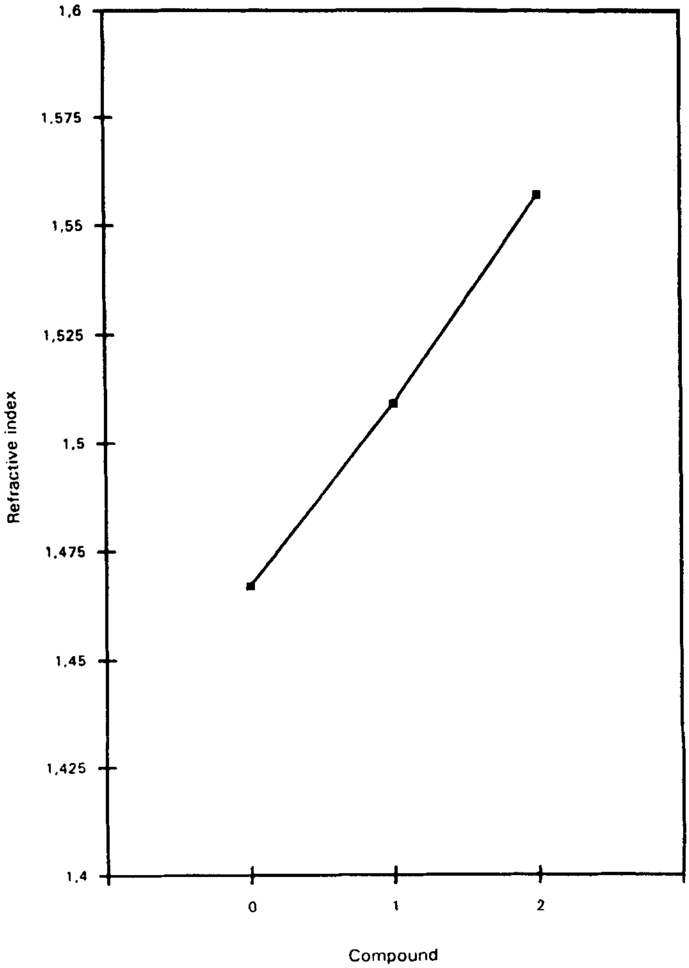


FIG. 7. Comparison of the refractive indices (n_D^{20}) of POE-A and the telechelic compounds **1** and **2**.

Thin-layer chromatographic investigations of the educt and the three products **1**, **2**, and **3** are documented in Fig. 6. It is shown that the distribution pattern of the molar masses is not significantly altered during the terminal transformation reactions and the precipitation procedures. The influence of the molar mass on the refractive index is shown in Fig. 7. It can be seen that an increasing molar mass results in higher values of the refractive index.

Due to the high solubilizing power of the poly(oxyethylene) chain it is possible to obtain telechelic derivatives with condensed aromatic compounds although those often exhibit a very poor solubility in many solvents. This is confirmed by the fact that comparable compounds, e.g., 1,6-hexane diacid 2-anthracenyl diamide, were found to be insoluble in most solvents [19]. Such anthracene-terminal telechelics represent interesting intermediates as building blocks for copolymers, crosslinkers for polymer matrices, and reagents for graft polymers.

The results confirm the amide formation of poly(oxyethylene) carboxylic acid with aromatic amines to be a convenient and efficient approach to the introduction of aromatic end-groups into telechelics. These telechelics open access to a number of secondary derivatives by electrophilic aromatic substitutions and Diels-Alder reactions.

Whereas naphthalene is quite resistant to Diels-Alder attacks, anthracene gives Diels-Alder reactions readily. Therefore, telechelic anthracene derivatives are suitable diene components for Diels-Alder reactions and react very easily with a variety of dienophiles. This might be an interesting concept to give Diels-Alder products with a variety of dienophiles for the preparation of new materials on the basis of telechelic Diels-Alder adducts. As such reactions are easy, quick, and of very broad scope [20, 21], the employment of the new poly(oxyethylene) telechelics can be envisaged as telechelic trapping reagents for a variety of dienophiles.

CONCLUSION

Starting from α,ω-di(carboxymethylene) poly(oxyethylene), telechelic compounds with three different unsubstituted aromatic end-groups were prepared. Thus, the aromatic amines aniline, 2-naphthylamine, and 2-aminoanthracene were reacted with telechelic poly(oxyethylene) diacarboxylic acid to produce the corresponding amide telechelics. The new compounds were characterized by several spectroscopic methods and are important building blocks for the preparation of hydrophilic polymers and new materials.

ACKNOWLEDGMENT

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