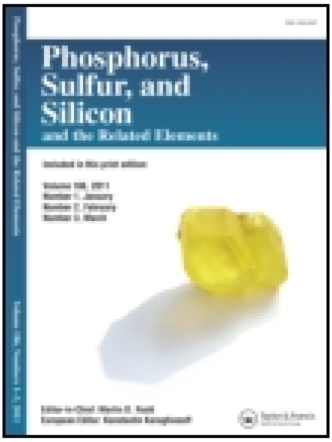

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Synthesis and Properties of Long-Chain Aromatic Telechelic Monodispersed Diols Radical-Initiated, Addition of 2-Mercaptoethanol onto α, ω Nonconjugated Dienes

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SYNTHESIS AND PROPERTIES OF LONG-CHAIN AROMATIC TELECHELIC MONODISPERSED DIOLS RADICAL-INITIATED, ADDITION OF 2-MERCAPTOETHANOL ONTO α, ω NONCONJUGATED DIENES

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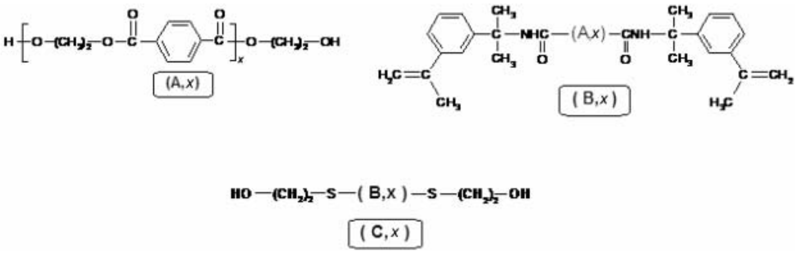
GRAPHICAL ABSTRACT



Abstract *The synthesis of aromatic telechelic mono dispersed diols produced from the radical-initiated addition reaction of a twofold excess of 2-mercaptoethanol onto original* α,ω *nonconjugated dienes reaction is presented. These novel* α,ω *nonconjugated dienes were prepared by addition reaction of m-isopropyl* α,α' *dimethyl benzylisocyanate with mono dispersed telechelic diols obtained by fractionation of oligo(ethylene terephthalate)s. In these cases, the long chain* α,ω *diols were produced selectively and quantitatively. The products are soluble in most organic solvents in contrast to classical oligo (ethylene terephthlate)s and posses a lower glass transition and melting temperatures.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *for the following free supplemental resource: Figures S1-S3.*

Keywords α, ω nonconjugated dienes; 2-mercaptoethanol; telechelic monodispersed diols; polyurethanes; thermal properties; solubility

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INTRODUCTION

Telechelic polymers are generally moderate molecular weight polymers that bear functional groups at both chain ends. They are characterized by the nature and the number of those functional groups. The first, and still most important, interest of telechelics comes from the fact that functional end groups can be involved in coupling reactions, leading to block copolymers, polymers networks, segmented polymer networks, and soft polymer networks.[1–5] On the industrial scale, several materials are produced. Among them, the oldest and most important ones are the polyurethane's synthesized from coupling telechelic hydroxy polymers with α,ω- diisocyanates.

The polyurethanes are produced with an extremely wide range of physical and chemical properties.[6–10] Telechelics have been also used for the synthesis of linear segmented copolymers leading to many new materials with various properties obtained by appropriate combinations of soft and hard segments. These telechelics are the basis of the development of the thermoplastics elastomers.[11,12] New developments in this field are obtained by exploration of combination of telechelics with exceptional properties such as low glass transition temperature, high melting temperatures increased thermal stabilities, liquid crystalline properties, and dynamic mechanical thermal characteristics.[13–15]

Telechelic or α,ω-difunctional precursors are required to obtain high molecular weight materials with satisfactory properties. Synthesis and use of fluorinated or hydroxy polybutadienes telechelics were described, their properties were also investigated.[16,17] Telechelic diols are important precursors for polycondensates, such as polyesters, polyurethanes, polycarbonates, and silicones, and can also be used to introduce photocrosslinkable functions into polymeric systems. In addition they can full in a wide range of recent applications.[18–24] Long hydrocarbon chain ethers and ketones with bis-terminated hydroxy or carboxyl groups have been synthesized and evaluated for their potential to favorably alter lipid disorders including metabolic syndrome.[25]

Interestingly, recent investigations have shown that both mechanical properties of the resulting polyurethanes[26,27] and their thermostability[28–31] were improved when a monodispersed diol was used compared to a polydispersed one.[32] Long-chain heteroatom containing telechelic diols were synthesized with well-defined end group reactivity, and are well suited for the preparation of high molecular weight block copolymers.[33–35] It was also noted that the radical telomerization[23,27–30] was more adequate than the redox one [36–38] or any other conventional techniques[38,39] to produce such compounds selectively and in high yields.

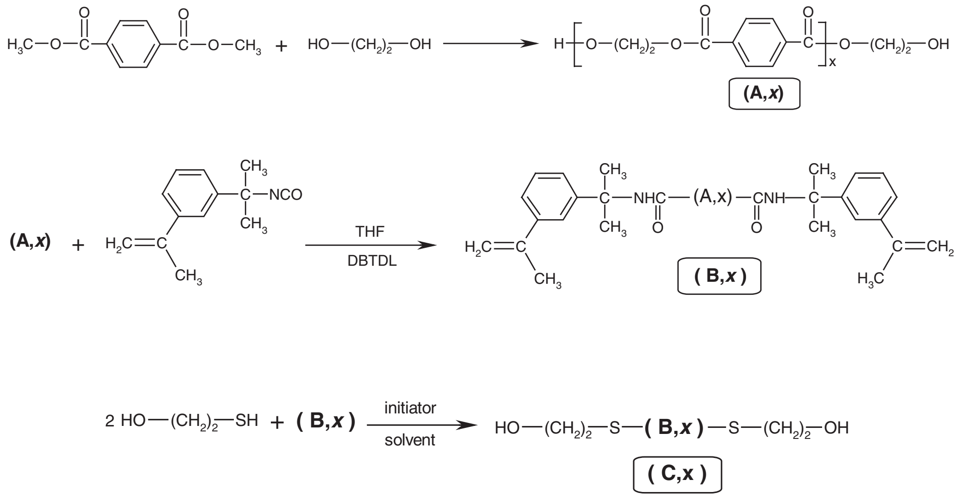
In the case of the radical monoaddition of undecenic derivatives with α,ω-dithiols, improving their solubility, polar groups could be introduced either from the monomer[27–30] or the dithiols.[29] Previous structures mainly involved aliphatic derivatives.

However, only a few research articles have mentioned the synthesis of aromatic telechelic monodispersed diols.[39–45] Hence, it was interesting to prepare such compounds from the same above pattern that involves aromatic α,ω-dienes prepared by addition of oligo (ethylene terephthalate) to commercially available m-isopropyl α,α'-dimethylbenzyl isocyanate.[32,46]

Moreover, the literature mentions that polydispersed ethylene terephthalate polymers are available and usually they are prepared according to different methods (polytransesterification,[47–49] polyesterification,[50–54] and polycondensation[55–62]). These methods require two steps, and sometimes it is difficult to control their kinetics.[48,49] Thus, it was of interest to prepare similar compounds bearing different functions on their backbone with a new method.

RESULTS AND DISCUSSION

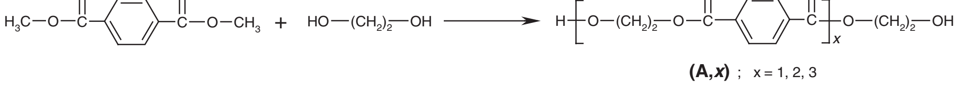
The syntheses of long chain aromatic telechelic monodispersed diols were performed by radical addition of 2-mercaptoethanol with telechelic dienes [(B, 1), (B, 2), (B, 3)] according to Scheme 1, in which the synthesis of ethylene terephthalate oligomers is first described.



Scheme 1

Synthesis of Oligo (Ethylene Terephthalete)s

It is known that the preparation of oligo (ethylene terephthalate) can be achieved by polytransesterification,[34–36] by polyesterification,[37–42] and by polycondensation.[30,31] In this present case, we have chosen to prepare ethylene terephthalate oligomers by transesterification of dimethyl terephthalate and ethylene glycol as per Scheme 2.



Scheme 2

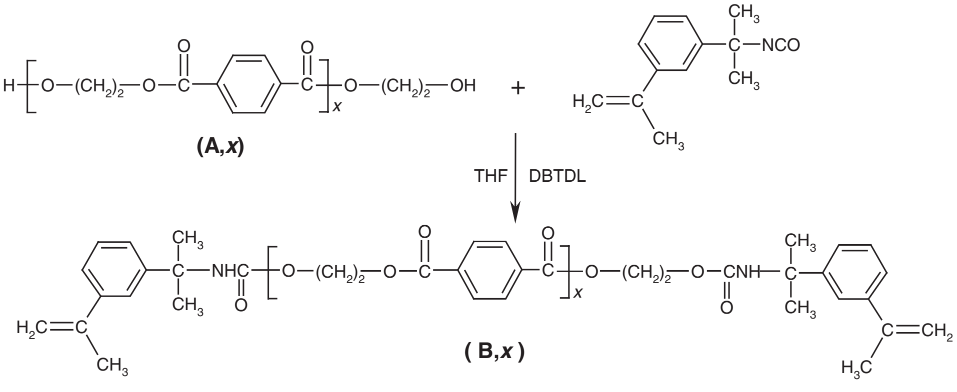
The different low molecular weight oligomers can be separated by fractionated precipitation and the first two products were obtained owing to their solubility into boiling water and THF, respectively. Both of them were easily identified by size exclusion chromatography and were characterized by IR and NMR. The IR spectra show expected broad bands at 3400–3600 cm^{-1} assigned to the hydroxy groups and sharp frequency at 1700 cm^{-1} for the carbonyl of ester function. The ^1H NMR spectra exhibit a singlet at 8.15 ppm characteristic of the aromatic ring whereas both methylene groups in the α and β positions that represent the hydroxy end groups gave triplets at 3.75 and 4.35 ppm, respectively; the singlet centered at 4.70 ppm corresponds to both methylene groups located between the terephthalic groups.

The signals centered at about 134 and 165 ppm in ^{13}C NMR spectrum of (A, 1) are characteristic of both different aromatic carbon atoms and to the carbonyl groups, respectively. Those at 59 and 67 ppm correspond to the methylene groups while that adjacent to the ester function is low field shifted. The signal at 63 ppm in the ^{13}C NMR spectrum of the dimer is assigned to methylene group located between the aromatic rings.

The insolubility of the diol (A, 2) inhibits the preparation of (A, 3), and its condensation between terephthaloyl chloride was unsuccessful. Thus, from the above results, it is noted that the increase of the length of alkylenic chain of terephthalate oligomers improves their solubility. Ester functions also contribute to such an improvement although their effect seems slightly less important.

Synthesis of Aromatic Telechelic Nonconjugated Monodispersed Dienes (B, *x*)

The synthesis of aromatic telechelic nonconjugated monodispersed dienes was performed by the addition reaction of oligo (ethylene terephthalate) to the monoisocyanate (m-isopropyl- α,α'- dimethylbenzyl) isocyanate according to Scheme 3.



Scheme 3

The reaction was catalyzed by the dibutyl tin dilaurate (DBTDL) and was monitored by FTIR. It was stopped when the frequency band of the NCO function at 2270 cm^{-1} disappeared. The IR spectra of the dienes (B, *x*) exhibit the presence of a band at 1720 cm^{-1} assigned to the vibration of the urethane group (–OCONH–) free from hydrogen bonding, and the absence of any broad band in the 3400–3600 cm^{-1} range characteristic of hydroxy group. The dienes were characterized by means of ^{1}H and ^{13}C NMR. The ^{1}H NMR spectra of these compounds show

- the absence of signals assigned to the hydroxy protons of telechelic diols;
- the presence of two singlets centered at $\delta = 5.00$–5.35 ppm of ethylenic aromatic bonding; and
- a new signal appears at 5.60 ppm attributed to the proton of (—NHCOO—) aliphatic urethane group.

The ^{13}C NMR spectra show a characteristic signal centered at 165 ppm of the carbonyl urethane group. The ester carbonyl leads to a signal at 165.3 ppm. The most important was

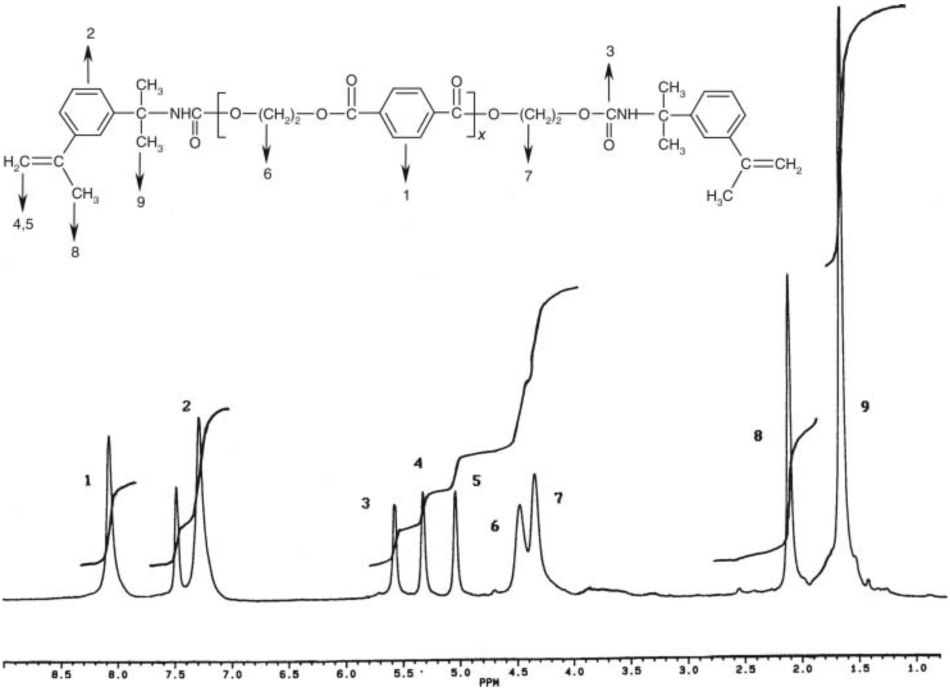


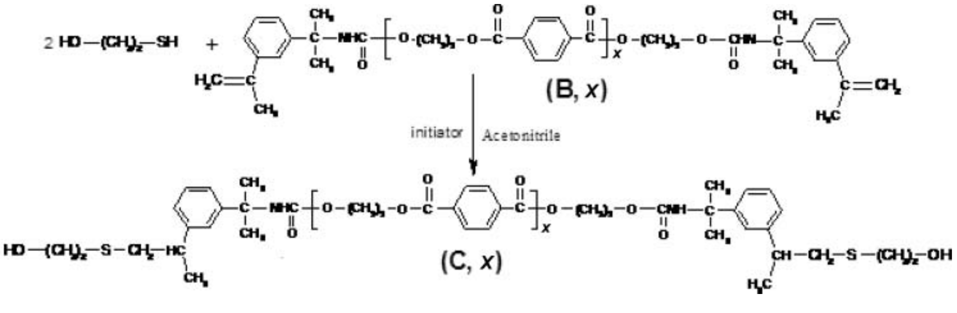
Figure 1 ^{1}H NMR spectrum of (B, 2).

the obtention of telechelic nonconjugated monodispersed dienes with yields higher than 90% using simply an addition reaction. IR, ^{1}H, and ^{13}C NMR characteristics are detailed in the experimental part. Figure 1 shows the ^{1}H NMR spectrum of Bis[2-(m-isopropyl α,α'-dimethylbenzylcarbamoyl) ethoxy terephthaloyloxy] ethyl (B, 2)

Synthesis of Long Chain Monodispersed Diols

The radical initiated addition of thiol to dienes was previously described,[17–19] and it was shown that radical initiation in the presence of peroxides was the most adequate to produce the expected diols in quantitative yields.[17,18]

The synthesis of aromatic monodispersed diols was performed under similar conditions from the radical bis-monoaddition of 2-mercaptoethanol onto a long chained nonconjugated telechelic monodispersed dienes as per Scheme 4.



Scheme 4

First, a model reaction was carried out with a telechelic diene produced from low molecular weight oligo (ethylene terephthalate), (case where $x = 1$). Such a reaction involved the initial molar ratios (R_0 and C_0) $[\text{thioalcohol}]_0/[\text{telechelic diene}]_0$ and $[\text{initiator}]_0/[\text{telechelic diene}]_0$ of 2 and 0.02, respectively. Tertbutyl peroxypivalate was chosen as the initiator.[18] The reactions were carried out at 70 °C for 4 h and monitored by size exclusion chromatography. After the reaction, the diol was precipitated twice and then recrystallized from methanol. The resulting diol was characterized by IR and NMR spectroscopy.

The IR spectrum of (C, x) showed the absence of the band corresponding to an olefenic group at 1640 cm^{-1}, but the presence of a broad band at about 3500 cm^{-1} assigned to the vibration of the hydroxy groups. The ^1H NMR spectrum exhibits the absence of signals corresponding to ethylenic protons and of mercapto function at 5.00–5.35 and 1.95 ppm, respectively. The presence of a broad singlet centered at 1.60 ppm corresponded to the methylenic chain and of triplets at 2.75 ppm and 3.50 ppm was assigned to methylene groups adjacent to sulfur atoms and to the hydroxy end groups, respectively. The other signals are similar to those of the corresponding telechelic dienes. It was noted that the RS° radical produced in the initiation step has reacted with the less hindered side of the double band as observed previously[17,18,42,43] or in work performed by Nuyken[44,45] or Klemm.[46,47]

The ^{13}C NMR spectrum exhibits the expected singlets corresponding to the different carbon atoms of diol (C, 1). As indicated in the experimental part, it does not show any ethylenic atoms at 115 and 139 ppm assigned to ethylenic carbon of telechelic dienes. They are in good agreement with different peaks predicted by others authors.[48,49] Such a diol was obtained quantitatively and selectively (i.e., α- monoaddition).

The synthesis of other diols (C, x), $x = 2, 3$, was performed in similar conditions as described above in the presence of initiator. Each SEC curve of the produced diol shows a unique sharp peak. The expected diols were obtained selectively and in yields higher than 90%. Figure 2 shows the ^1H NMR spectrum of Bis{2-[m-(2-hydroxyethylthiaisopropyl)α,α'-dimethylbenzyl-carbamoyl]ethoxyterephthaloyloxy} ethyl (C, 2).

Physical Properties of Diols (C, *x*)

The solubility and the thermal characteristics (melting and glass transition temperatures) of the different long-chained aromatic diols were studied.

Solubility: It was observed that oligo (ethylene terephthalate) being polydispersed or fractionated (i.e., monodispersed) is partially soluble in common organic solvents, except in THF. However, when these substances are functionalized with mercapto groups, the ester function confers to the corresponding compounds an improved solubility.

Furthermore, all diols produced by radical bis monoaddition of 2-mercaptoethanol onto telechelic dienes exhibit a very good solubility in most organic solvents at room temperature. The best nonsolvent to favor their precipitation and their purification was fluorinated solvents, e.g., $CF_3CH_2CF_2CH_3$ and $ClCF_2CFCl_2$. This good solubility arises from the presence of a polar function such as an ester group, which favored hydrogen bonding.

Melting and Glass Transition Temperature

Table 1 lists the glass transition (Tg) and melting temperatures (Tm) of oligo (ethylene terephthalate)s and those of the corresponding diols, determined by means of calorimetry.

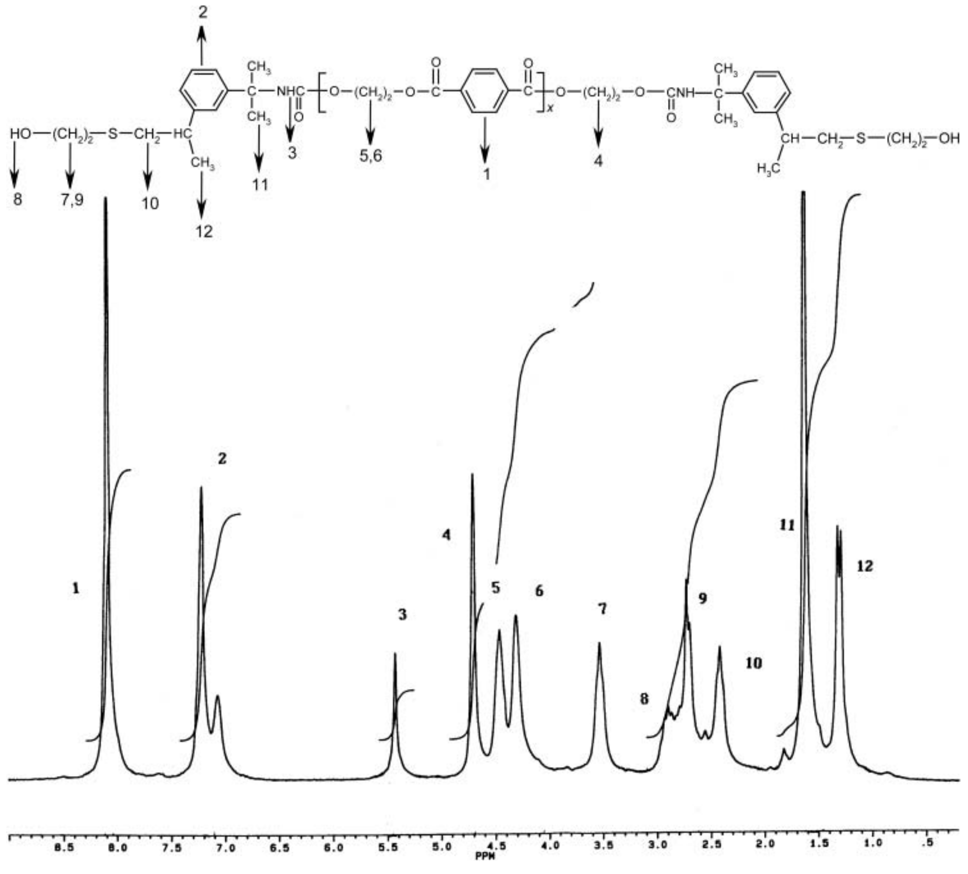


Figure 2 ^{1}H NMR spectrum of (C, 2).

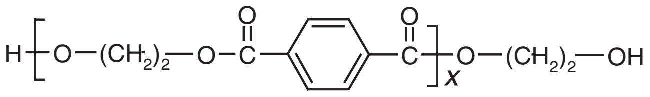
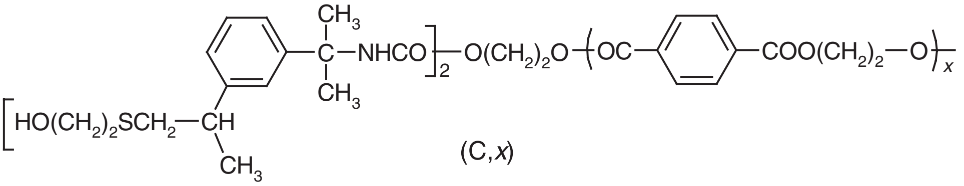
It is observed that oligo (ethylene terephthalate)s do not exhibit any glass transition temperature but their melting temperatures are high. It is observed too that for the same degree of polymerization, the *Tm* decrease when the length of methylenic chain increase. *Tm* of oligo(tetramethylene terephthalate) < *Tm* of oligo (ethylene terephthalate).[42]

However, each corresponding diol produced from the radical bis monoaddition of 2-mercaptoethanol onto α, ω-telechelic diene exhibits a semicrystalline behavior evidenced by a sharp endotherm. It seems that such substances also exhibit amorphous zones as evidenced by the presence of a jump in heat capacity assigned to a glass transition temperature.

More interesting, the *Tm* of such diols is much lower than those of the starting diols (about 70 °C–100 °C). It is considered that the polar ester groups stiffen the molecules, but the long methylenic chain increases their softness as if is evidenced by a low *Tg*. This is in agreement with previous investigations.[20,42]

Moreover, from Table 1, it is noted for the same terephthalate series that the values of both *Tg* and *Tm* temperatures increase when the degree of polymerization of diols (C, *x*) increases too. The aromatic groups in these compounds became higher. Furthermore, it was observed that for the same degree of polymerization[18] the diols produced from monodispersed oligo(tetramethylene terephthalate)s exhibit lower *Tg* and *Tm* values than

Table 1 Molecular weights (M^a, M^b, M^c), melting (Tm), and glass transition (Tg) temperatures of telechelic diols (A, x) and (C, x). M^a: molecular weights theoretically expected; M^b: calculated from OH titration; M^c: determined from 1H NMR

(A, x) and (C, x)	M^a	M^b	M^c	Tm/°C	Tg/°C
 (A,x)					
(A, 1)	254	nd	250	109	none
(A, 2)	446	nd	440	169	none
(A, 3)	639	nd	640	199	none
(A, ∞)	—	—	—	67–125[63]	250–310[63]
 (C,x)					
(C, 1)	812	790	800	71	−9
(C, 2)	1004	980	990	113	11
(C, 3)	1196	1150	1170	123	15

those of oligo (ethylene terephthalate)s starting materials. This behavior arises from the tetramethylene groups, which bring softness into these molecules.

EXPERIMENTAL PART

Materials

The starting materials were purchased from Aldrich and did not require further purification prior to use; the m-isopropyl α, α'-dimethyl benzylisocyanate (m-TMI) was delivered from Cyanamid Company. The reactions were monitored by size exclusion chromatography (SEC) using a Waters Associates apparatus equipped with a Knauer HPLC (Model 64) pump; tetrahydrofuran (THF) was used as the eluent (flow rate 1.5mL/min at 30 °C). The separation was carried out with a set of four Polymers Lab columns, the pore diameters of which were 10.000, 1000, 500, and 100 Å. The detection was performed with a Knauer differential refractomer, and Fourier transform infrared (FTIR) spectra were conducted with a Nicolet 510 (P) spectrometer. The accuracy of the bonds was given with an error of ± 2.0 cm^{-1} and the letters VS, S, M, or W indicate Very Strong, Strong, Medium, or Weak intensity, respectively. The different pure telomers were characterized by ^{1}H and ^{13}C NMR spectroscopy at room temperature. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 250, AC 200, or CW 360, by using deuterated chloroform ($CDCl_3$) as the internal reference and solvent, respectively. The letters: s, d, t, q, and m designate singlet, doublet, triplet, quadruplet, and multiplet, respectively. DSC scans for compounds C1, C2, and C3 are located in the Supplemental Materials (Figures S 1–S 3).

Differential scanning calorimetry (DSC) measurements were conducted with a PerkinElmer DSC 4 apparatus equipped with a TADS microcomputer; the apparatus was calibrated with indium that has a melting temperature of 156.6 °C and an enthalpy of fusion of 28.5 J/g. A first scan was conducted at a heating rate of 40 °C/min up to 100 °C, it was then quenched to −70 °C, and left for 5 min at that temperature before a second scan at heating rate of 10 °C/min, this gave the glass transition temperature (*Tg*) values reported in this paper, taken at half height of the jump in the heat capacity at the glass transition, and those of melting temperature (*Tm*) corresponds to the value of the maximum of the endothermic peak. The hydroxy end groups were titrated with an acetic anhydride/pyridine mixture. The residual acetic acid was titrated with sodium hydroxide.

Synthesis of Telechelic Monodispersed Diols: Ethylene Terephthtalate Oligomers

In a two-necked round-bottom flask equipped with a condenser and a distillation device, dimethyl terephthalate and an excess of ethylene glycol in a 1:12 molar ratio were introduced.

Zinc acetate (100 mL of ethylene glycol; 0.4 mmol) was added as a catalyst and chloroacetic acid (250 mL of ethylene glycol; 1 mmol) was added to prevent the catalyst from being inhibited. Methanol was recovered by distillation. The mixture was cooled and dropwise added into deionized water, and the precipitate was heated up to 70 °C for 24 h under vacuum. The mixture was heated up to 100 °C and quickly filtered to separate diol DP_3, soluble in boiling water. Then, this filtrate was cooled down to 10 °C and the crystals were dried under pressure at 80 °C.

Bis (2-hydroxyethyl) Terephthalate (A, 1). $Tm = 109$ °C, no *Tg* was observed by DSC. IR (KBr, cm^{-1}): 3600–3200 (S, broad); 2950 (S); 2890 (M); 1950 (W); 1700 (VS); 1500 (W); 1450 (M); 1400 (S); 1270 (VS); 1140 (S); 1070 (S); 1020 (S); 900 (S); 870 (M); 840 (M); 730 (S); 500 (M). ^1H NMR (DMSO d_6) δ: 3.75 (m, 4H); 4.50 (t, 4H); 5.00 (t, 2H); 8.15 (s, 4H). ^{13}C NMR (DMSO d_6) δ: 59.2; 67.1; 129.5; 133.8; 165.3; $C_{12}H_{14}O_6$ (254.24). Calculated: C (56.69), H (5.55); Found: C (57.08), H (5.28). Diol DP_5 is soluble in boiling THF; hence, it can be separated from the higher molecular weight diols. White powder was obtained.

Bis (2-hydroxyethoxy Terephthaloyloxy) Ethyl (A, 2). $Tm = 169$ °C, no *Tg* was observed by DSC. IR (KBr, cm^{-1}): 3600–3200 (S, broad); 2950 (S); 2890 (M); 1960 (W); 1700 (VS); 1500 (W); 1450 (W); 1410 (M); 1340 (M); 1270 (VS); 1130 (S); 1070 (S); 1020 (M); 900 (M); 870 (M); 830(W); 730 (VS); 500 (M). ^1H NMR (DMSO d_6) δ: 3.75 (t, 4H); 4.35 (t, 4H); 4.70 (s, 4H); 5.00 (t, 2H); 8.15 (s, 8H). ^{13}C NMR (DMSO d_6) δ: 56.2; 59.1; 63.3; 129.6; 129.7; 133.4; 134.0; 165.1; 165.2; $C_{22}H_{22}O_{10}$ (446.41). Calculated: C (59.19), H (4.97); Found: C (59.93), H (4.71).

Synthesis of Higher Boiling-Point Oligo (Ethylene Terephthalate) (A, 3). In a three-necked round-bottom flask equipped with a condenser, a dropping funnel and saturated with a nitrogen flow were introduced terephthaloyl chloride and diol (A, 1) in an initial mole ratio 1:6. THF was used as the solvent. Pyridine was added to such a mixture in a 2:1 mole ratio with a reference to diol (A, 1). The medium was refluxed for 4 h and then the warmed white solid produced was filtered off twice and washed. It was recrystallized from DMSO.

Bis [2-(2-hydroxyethoxy Terephthaloyloxy) Ethyl] Terephthalate (A, 3). $Tm = 199$ °C, no *Tg* was observed by means of DSC. IR (KBr, cm^{-1}): $\nu = 3600$–3200 (S, broad); 2940 (S); 2880 (M); 1960 (W); 1700 (VS); 1520 (W); 1460 (W); 1420 (M); 1340 (M); 1280 (VS); 1130 (S); 1070 (S); 1030 (M); 900 (M); 880 (M); 850 (W); 730 (VS); 490

(M). ^{1}H NMR (DMSO d_6) δ: 3.75 (m, 4H); 4.35 (m, 4H); 4.70 (m, 8H); 4.90 broad signal shifted with dilution (m, OH, 2H); 8.15 (s, aromatic protons, 12H). ^{13}C NMR (DMSO d_6) δ: 56.2; 59.1; 63.3; 129.6; 129.7; 133.4; 134.0; 165.1; 165.2; $C_{32}H_{30}O_{14}$ (638.58). Calculated: C (60.19), H (4.74); Found: C (61.28), H (4.56).

Synthesis of Aromatic Telechelic Monodispersed Dienes

Synthesis from Oligo (Ethylene Terephthalate)s. All the experiments were performed under nitrogen using standard Schlenk techniques. THF was distilled by the usual methods[64] and stored under nitrogen. Typical procedure of the addition was as follows: in a Schlenk flask containing m-isopropyl α,α'- dimethylbenzylisocyanate was added, respectively, to a solution of monodispersed oligo (ethyleneterephthalate)s (A, 1), (A, 2), and (A, 3) in THF in a molar ratio 2:1 ([OH]/[NCO] = 1).

The DBTDL was added to the solution as a catalyst. The mixture was flushed with N_2 several times and was heated at 80 °C for 5 h under stirring. The reaction was stopped when the frequency absorption band in IR spectroscopy of NCO at 2270 cm^{-1} disappeared. The mixture was poured into methanol, which led to separation of the product. It was collected by filtration, washed with methanol, and dried under vacuum to give a series of monodispersed aromatic telechelic dienes (B, 1), (B, 2), and (B, 3). In each case, the yields were quantitative.

Bis [2-(m-isopropyl α,α'-dimethylbenzylcarbamoyl) Ethyl] Terephthalate (B, 1). *Tm* = not determined. IR (KBr, cm^{-1}): ν = 3360 (VS); 2920 (S); 2880 (M); 1720 (VS); 1660 (W); 1600 (M); 1580 (M); 1510 (S); 1450 (M); 1410 (M); 1390 (W); 800 (M); 735 (S); 700 (M). ^{1}H NMR ($CDCl_3$) δ: 1.60 (s, 12H); 2.10 (s, 6H); 4.30 (s, 4H); 4.45 (s, 4H); 5.60 (s, 2H); 7.25–7.45 (d, 8H); 8.10 (s, 4H); 5.05–5.35 (s, 4H, ethylenic protons). ^{13}C NMR ($CDCl_3$) δ: 59.2; 67.1; 129.6; 133.8; 165.3; $C_{38}H_{44}O_8N_2$ (656.74). Calculated: C (69.43), H (6.69), N (4.26); Found: C (70.50), H (7.10), N (4.50).

Bis[2-(m-isopropyl α,α'-dimethylbenzyl Carbamoyl) Ethoxy Terephthaloyloxy] Ethyl (B, 2). *Tm* = not determined. IR (KBr, cm^{-1}): ν = 3360 (VS); 2920 (S); 2880 (M); 1720 (VS); 1670 (W); 1610 (M); 1580 (M); 1500 (S); 1450 (M); 1410 (M); 1380 (W); 800 (M); 730 (S); 700 (M). ^{1}H NMR ($CDCl_3$) δ: 1.60 (s, 12H); 2.10 (s, 6H); 4.30 (s, 8H); 4.45 (s, 8H); 5.00–5.35 (s, 4H, ethylenic protons); 5.60 (s, 2H); 7.25–7.45 (d, 8H); 8.10 (s, 8H). ^{13}C NMR ($CDCl_3$) δ: 59.1; 63.2; 67.1; 129.6; 129.7; 133.4; 134.0; 165.1; 165.2; $C_{48}H_{52}O_{12}$ N_2 (848.48). Calculated: C (67.92), H (6.13), N (3.30); Found: C (68.10), H (6.60), N (3.50).

Bis{2-[2-(m-isopropyl α,α'-dimethylbenzyl Carbamoyl) Ethoxyterephthaloyloxy] Ethyl} Terephthalate (B, 3). *Tm* = not determined. IR (KBr, cm^{-1}): ν = 3360 (VS); 2920 (S); 2880 (M); 1710 (VS); 1675 (W); 1610 (M); 1580 (M); 1500 (S); 1450 (M); 1410 (M); 1380 (W); 800 (M); 730 (S); 705 (M). ^{1}H NMR ($CDCl_3$) δ: 1.60 (s, 12H); 2.10 (s, 6H); 4.30 (s, 4H); 4.45 (s, 4H); 5.00–5.35 (s, 4H; ethylenic protons); 5.60 (s, 2H); 7.25–7.45 (d, 8H); 8.10 (s, 8H). ^{13}C NMR ($CDCl_3$) δ: 59.2; 67.1; 129.5; 133.8; 165.3; $C_{58}H_{60}O_{16}$ N_2 (1040.58). Calculated: C (66.92), H (5.76), N (2.69); Found: C (67.20), H (5.95), N(2.96).

Synthesis of Long Chain Aromatic Telechelic Monodispersed Diols

These diols were all prepared in the same way according to the following experimental procedure: in a three-necked round-bottom flask equipped with a condenser and nitrogen flow, a mixture composed of 2-mercaptoethanol and (B, 1), (B, 2), (B, 3) in a 2:1 molar ratio was introduced and dissolved in acetonitrile as the solvent. This medium was heated up to 75 °C under stirring; then, AIBN was added into the flask in the [(initiator)/(telechelic diene)] molar ratio of 0.02. The solution was kept stirring at 75 °C under nitrogen for 4 h. The experiment was monitored using SEC and it was observed that, after 3 h, 90% of 2-mercaptoethanol was consumed. After the reaction was completed, the diol was precipitated and recrystallized from methanol. For all these syntheses, the yields of three diols were quantitative.

Bis{2-[m-(2-hydroxyethylthiaisopropyl)α,α'-dimethylbenzylcarbamoyl] ethyl}terephthalate (C, 1). $Tm = 71$ °C, $Tg = -9$ °C. IR (KBr, cm^{-1}): $\nu = 3600$–3000 (S, broad); 1720 (VS); 1520 (m); 1450 (W); 1280 (S); 1260 (S); 1240 (S); 1120 (M); 1100 (S); 1020 (M); 880 (W); 740 (S); 710 (M). ^1H NMR ($CDCl_3$) δ: 1.30 (d, 6H); 1.60 (s, 12 H); 2.40 (m, 4H); 2.75 (m, 4H); 2.85 (m, 2H); 3.50 (t, 4H); 3.90 (t, 2H); 4.30 (s, 4H); 4.45 (s, 4H); 4.70 (s, H); 5.40 (s, 2H); 7.05–7.20 (d, 8H); 8.10 (s, 4H). ^{13}C NMR ($CDCl_3$) δ: 20.7; 22.5; 28.8; 29.2; 35.0; 40.3; 55.0; 60.2; 60.8; 61.8; 62.9; 63.6; 66.8; 122.3; 123.5; 125.0; 128.2; 129.5; 133.4; 133.6; 133.9; 145.2; 147.0; 154.2; 165.3; 165.6; $C_{42}H_{56}O_8$ N_2 S_2 (812.74). Calculated: C (62.01), H (6.89), N(3.44); Found: C (62.45), H (7.15), N (3.50).

Bis{2-[m-(2-hydroxyethylthiaisopropyl)α,α'-dimethylbenzylcarbamoyl] ethoxyterephthaloyl-oxy} Ethyl (C, 2). $Tm = 113$ °C, $Tg = 11$ °C. IR (KBr, cm^{-1}): $\nu = 3600$–3000 (S, broad); 1720 (VS); 1520 (M); 1450 (W); 1280 (S); 1260 (S); 1240 (S); 1120 (M); 1100 (S); 1020 (M); 880 (W); 740 (S); 710 (M). ^1H NMR ($CDCl_3$) δ: 1.30 (d, 6H); 1.60 (s, 12H); 2.40 (m, 4H); 2.75 (m, 4H); 2.85 (m, 2H); 3.50 (t, 4H); 3.90 (t, 2H); 4.30 (s, 8H); 4.45 (s, 4H); 4.70 (s, H); 5.40 (s, 2H); 7.05–7.20 (d, 8H); 8.10 (s, 8H). ^{13}C NMR ($CDCl_3$) δ: 20.7; 22.5; 28.8; 29.2; 35.0; 40.3; 55.0; 60.2; 60.8; 61.8; 62.9; 63.6;66.8; 122.3; 123.5; 125.1; 128.2; 129.6; 133.4; 133.6; 133.9; 145.2; 147.0; 154.2; 165.3; 165.6; $C_{52}H_{64}O_{13}$ N_2 S_2 (1004.05). Calculated: C (62.12), H (6.37), N (2.78); Found : C (62.50), H (6.60), N (2.95).

Bis(2-{2-[m-(2-hydroxyethylthiaisopropyl) α,α'-dimethylbenzylcarbamoyl] Ethoxy Terephthaloyl-oxy} Ethyl) Terephthalate (C, 3). $Tm = 123$ °C, $Tg = 15$ °C. IR (KBr, cm^{-1}): $\nu = 3600$–3000 (S, broad); 1720 (VS); 1520 (M); 1450 (W); 1280 (S); 1260 (S); 1240 (S); 1120 (M); 1100 (S); 1020 (M); 880 (W); 740 (S); 710 (M). ^1H NMR ($CDCl_3$) δ: 1.30 (d, 6H); 1.60 (s, 12H); 2.40 (m, 4H); 2.75 (m, 4H); 2.85 (m, 2H); 3.50 (t, 4H); 3.90 (t, 2H); 4.30 (s, 12 H); 4.45 (s, 4H); 4.70 (s, H); 5.40 (s, 2H); 7.05–7.20 (d, 8H); 8.10 (s, 12H). ^{13}C NMR ($CDCl_3$) δ: 20.7; 22.5; 28.8; 29.2; 35.0; 40.3; 55.0; 60.2; 60.8; 61.8; 62.9; 63.6; 66.8; 122.3; 123.5; 125.0; 128.2; 129.5; 133.4; 133.6; 133.9; 145.2; 147.0; 154.2; 165.3; 165.6; $C_{62}H_{72}O_{18}$ N_2 S2 (1196.58). Calculated: C (62.17), H (6.01); N (2.34); Found: C (63.20), H (6.70), N (2.65).

CONCLUSION

The synthesis of telechelic aromatic monodispersed diols with molecular weights between 800 and 1200 g/mol can be simply achieved by the bis monoaddition of telechelic aromatic monodispersed dienes with 2-mercaptoethanol, initiated with azoïques and peroxides. Such reactions are quick, easy to perform and to scale up, and lead to the diols in quantitative yields.

These diols are soluble in most organic solvents. They exhibit a semicrystalline behavior with lower melting temperature than those of oligo(ethylene terephthalate). The telechelic aromatic monodispersed dienes were produced by addition reaction of m-isopropyl α, α' dimethyl benzylisocyanate to oligo (ethylene terephthalate). The latter compounds were obtained by esterification of dimethyl terephthalate with ethylene glycol, followed by fractionation. Such aromatic telechelic long-chain diols are interesting precursors of well-defined architectured polymers such as the polyesters polycarbonates or polyurethanes.

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