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Preparation and characterization of poly(ε-caprolactone)-*b*-polyacrylonitrile (PCL-*b*-PAN) and poly(L-lactide)-*b*-polyacrylonitrile (PLLA-*b*-PAN) copolymers by aluminum and lithium alkoxides containing double-headed initiators

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Abstract

Three new metal alkoxides, $[(MMPEP)Al(\mu\text{-}OCH_2C_6H_4CH_2Cl)]_2$ (**1**), $[(MMPEP{-}H)Li\cdot(BnOH)]_2$ (**2**) and $[(MMPEP{-}H)Li\cdot(HOCH_2C_6H_4CH_2Cl)]_2$ (**3**) ($MMPEP{-}H_2$: 2,2′-methylene-bis{4,6-di(1-methyl-1-phenylethyl)phenol}) have been synthesized and characterized. Complex **1** was prepared by the reaction of $[(MMPEP)Al(CH_3)(Et_2O)]$ with *p*-(chloromethyl)benzyl alcohol. Followed by the reaction of $MMPEP{-}H_2$ with ^{n}BuLi, BnOH or *p*-(chloromethyl)benzyl alcohol was added to give complexes **2** and **3**, respectively. Complex **1** has shown excellent catalytic activity towards ring-opening polymerization (ROP) of ε-caprolactone. Both complexes **2** and **3** are active for ROP of L-lactide. Block copolymers of poly(ε-caprolactone)-*b*-polyacrylonitrile (PCL-*b*-PAN) and poly(L-lactide)-*b*-polyacrylonitrile can be synthesized by combining a technique of atom transfer radical polymerization (ATRP) and ROP using a double-headed initiator. Microphase-separated morphology of PCL-*b*-PAN has been observed by transmission electron microscopy, indicating the formation of self-assembled nanostructure.

Keywords: Double-headed initiator; ε-Caprolactone; L-Lactide

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1. Introduction

Nowadays, carbon materials have been used for a wide range of applications such as for chemistry, chemical engineering or material science. These materials can be applied in separation processes, electrochemistry, catalysis, energy/conversion devices, etc. [1]. Polyacrylonitrile (PAN) is one of the many materials used for manufacturing activated carbon [2] and is an important source for carbon fibers and carbon materials. Over the last decades, carbon material has played an important role in nanoapplications. The formation of carbon nanotube with regular textured and with proper orientations is expensive, tricky and complicate procedures, however, it is generally prepared either by physical/chemical vapor deposition techniques [3]. Recently, demands for developing new carbon materials have dramatically increased with high performance-to-price ratio. Therefore, it is a great challenge to explore an easy and cheap alternative method by adopting a mild reaction condition to synthesize carbon nanomaterials. Many technologies have been evolved for creating nanotemplates which have a great potential for the preparation of many nanomaterials. One of the most convenient ways for the preparation of nanotemplates is by self-assembling of diblock copolymers [4]. A variety of nanotemplates with different applications have received great interest nowadays, in general they can be obtained by simply controlling the fraction of constituted building blocks [5].

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Block copolymers with biodegradable polyester and polyacrylonitrile are good precursors for the preparation of carbon nanomaterials. A novel route based on block copolymer constituting a well-known carbonization precursor, such as poly(acrylonitrile), has been developed to generate a well-defined nanostructured carbon materials [6–9]. Copolymer of poly(ε-caprolactone) and poly(styrene-*co*-acrylonitrile) has been synthesized by blending method [10]. The preparation of homo- and copolymer polyacrylonitrile was typically carried out via free radical polymerization and anionic polymerization without having control on the molecular weight and its polydispersity indexes as well as other functional properties [11]. Matyjaszewski and coworkers have recently communicated the synthesis of polyacrylonitrile by using atom transfer radical polymerization (ATRP) technique. ATRP has more advantages for controlling polymer properties as compared to other analogue synthetic methods [12]. The typical method to synthesize poly(cyclic esters) is by the ring-opening polymerization [13–18]. With the help of this method, the molecular weight of the polymer can be controlled, and the PDIs are in a narrow range [19]. Therefore, we report herein the synthesis of aluminum and lithium complexes containing double-headed initiators [20] for the preparation of block copolymers with well-defined architectural properties.

2. Experimental section

2.1. General

All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing at least for 24 h over sodium/benzophenone (toluene, *n*-hexane and diethyl ether), phosphorus pentoxide (CH_2Cl_2), or over anhydrous magnesium sulfate (benzyl alcohol) and then freshly distilled prior to use. Deuterated solvents were dried over 4 Å molecular sieves. $[(MMPEP)Al(CH_3)(Et_2O)]$ [19c] and *p*-(chloromethyl)benzyl alcohol [21] were prepared according to literature method. Copper(I) bromide was purified by washing with pure acetic acid. Acrylonitrile, 2,2′-bipyridine, ethylene carbonate, NaOH, EDTA, MeOH and aluminum oxide (standard grade, ~150 mesh, 58 Å) were purchased and used as such without further purification. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or a Varian Unity Inova 600 MHz (the ^{13}C NMR spectra of complex **3**) spectrometer with chemical shifts given in parts per million from the internal standard TMS. Microanalyses were performed by using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent (for PCL and PLLA) or a Postnova PN1122 Solvent Delivery system equipped with a RI Detector PN3110 using DMF (HPLC grade) as an eluent (for PCL-*b*-PAN). Molecular weight and its distributions were calculated by using polystyrene as standard.

2.2. $[(MMPEP)Al(\mu\text{-}OCH_2C_6H_4CH_2Cl)]_2$ (**1**)

To an ice cold solution (0 °C) of $[(MMPEP)Al(CH_3)(Et_2O)]$ (1.57 g, 2 mmol) in toluene (20 mL) was added the solution of *p*-(chloromethyl)benzyl alcohol (0.312 g, 2 mmol) in toluene (10 mL). The mixture was stirred for 3 h while the temperature increased from 0 °C to room temperature and the volatile materials were removed under vacuum. The residue was redissolved in hot toluene and then concentrated to ca. 10 mL. The solution was allowed to cool to room temperature affording colorless crystalline solids after 24 h. Yield: 1.13 g (66%). ^1H NMR ($CDCl_3$, ppm): δ 6.69–7.28 (m, 56H, Ph), 4.27 (s, 4H, CH_2Cl), 3.19 (s, 4H, OCH_2), 2.37 (d, 2H, PhCH_2Ph, $J_{H-H} = 14.8$ Hz), 2.04 (d, 2H, PhCH_2Ph, $J_{H-H} = 14.8$ Hz), 1.82, 1.58, 1.57, 1.44 (s, 48H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 151.50, 151.13, 150.70, 140.48, 137.33, 136.47, 135.74, 129.24, 128.55, 128.22, 128.00, 127.82, 126.61, 126.51, 125.82, 125.64, 125.35, 125.30, 124.74 (Ph), 66.09 (OCH$_2$), 45.60 (CH$_2$Cl), 43.00, 42.25 (PhC(CH$_3$)$_2$Ph), 33.73, 31.04, 31.02, 30.73(C(CH$_3$)$_2$), 27.98 (PhCH$_2$Ph). IR (KBr, cm^{-1}): 3025 (m), 2965 (s), 2873 (m), 1597 (m), 1478 (s), 1373 (m), 1276 (s), 1203 (m), 1149 (m), 1093 (m), 1027 (m), 923 (m), 834 (m). Anal. Calcd. for $C_{114}H_{116}Al_2O_6Cl_2$: C, 80.21; H, 6.85. Found: C, 79.64; H, 6.22%. Mp = 184–186 °C.

2.3. $[(MMPEP\text{–}H)Li\cdot(BnOH)]_2$ (**2**)

To an ice cold solution (0 °C) of 2,2-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP–H_2) (2.70 g, 4.0 mmol) in diethyl ether (30 mL) was added benzyl alcohol (0.42 mL, 4 mmol). ^{n}BuLi (2 mL, 5 mmol in *n*-hexane) was then injected into the solution and the resulting mixture was stirred at room temperature for 3 h. The volatile materials were removed under vacuum and the residue was extracted in toluene (30 mL). The extract was concentrated to ca. 5 mL and *n*-hexane (ca. 50 mL) was added slowly. On keeping at room temperature for 24 h, white solid was obtained. Yield: 2.04 g (65%). ^1H NMR ($CDCl_3$, ppm): δ 6.78–7.37 (m, 58H, Ph), 5.10 (Br, 2H, PhOH), 4.63 (s, 4H, PhCH_2OH), 3.59 (s, 4H, PhCH_2Ph), 1.63, 1.54 (s, 48H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 151.67, 140.57, 139.37, 134.91, 129.50, 128.66, 128.39, 127.76, 127.51, 127.10, 127.00, 126.73, 126.43, 125.68, 125.23, 123.16 (Ph), 66.03 (OCH$_2$), 42.38, 42.10 (PhC(CH$_3$)$_2$Ph), 32.73, 31.07 (C(CH$_3$)$_2$), 29.83 (PhCH$_2$Ph). IR (KBr, cm^{-1}): 3500 (br), 2868 (m), 1599 (m), 1492 (s), 1462 (s), 1441 (s), 1381 (m), 1361 (m), 1319 (m), 1202 (m), 1030 (m). Anal. Calcd. for $C_{112}H_{118}Li_2O_6$: C, 85.46; H, 7.56. Found: C, 85.59; H, 7.55%. Mp = 143–145 °C.

2.4. $[(MMPEP\text{–}H)Li\cdot(HOCH_2C_6H_4CH_2Cl)]_2$ (**3**)

To an ice cold solution (0 °C) of 2,2-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP–H_2) (2.70 g, 4.0 mmol) and *p*-(chloromethyl)benzyl alcohol (0.624 g, 4.0 mmol) in diethyl ether (30 mL) was added slowly ^{n}BuLi