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ScienceDirect
Polymer Degradation and Stability 91 (2006) 3245−3251
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Thermal stability and high glass transition temperature of 4-chloromethyl styrene polymers bearing carbazolyl moieties

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Received 1 June 2006; received in revised form 5 July 2006; accepted 7 July 2006

Abstract

A new styrene derivative monomer, 4-(*N*-carbazolyl)methyl styrene (CzMS), was synthesized by reacting 4-chloromethyl styrene with carbazole in the presence of sodium hydride. Then, CzMS was homopolymerized and copolymerized with different monomers such as methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), ethyl acrylate (EA) and *n*-butyl acrylate (BA) by free radical polymerization method in *N*,*N*-di-methylformamide (DMF) solution at 70 ± 1 °C using azobisisobutyronitrile initiator to give the copolymers **I**−**V** in good yields. The structure of all the resulted polymers was characterized and confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. The average molecular weight and glass transition temperature of polymers were determined using gel permeation chromatograph (GPC) and differential scanning calorimeter (DSC) instruments, respectively. It was found that these polymers with carbazole moieties have high thermal stability and the presence of bulk carbazole groups in polymer side chains leads to an increase in the rigidity and glass transition temperature of polymers.

Keywords: 4-Chloromethyl styrene; Carbazole; Acrylic monomers; Chemical modification; Thermal stability; Glass transition temperature

1. Introduction

4-Chloromethyl styrene (CMS), or *p*-vinylbenzyl chloride (VBC), is one of the most important and interesting dual functional monomers. Due to the benzylic chlorine, a great number of nucleophilic substitutions are made possible, leaving the double bond undamaged and providing new monomers that can be polymerized or copolymerized when the experimental conditions are well chosen [1,2]. In addition, CMS can be easily polymerized or copolymerized with various initiators [3] and the obtained polymers are able to react with various nucleophilic reagents, giving fairly good yields in the process [4,5]. Functionalized poly(chloromethyl styrene) (PCMS) or related copolymers have been widely used in different processes as bactericide polymers [6], photo-sensitizers [7], solar energy storages [8], photo-resists [9], non-linear optics [10], cholesterol trapping of human serum [11] and prodrugs in biomedical applications [12].

Chemical modification of polymer structures is an important route for modification of polymer properties such as mechanical, thermal and surface properties. Therefore, PCMS or related copolymers are chemically modified by nucleophilic substitutions of the chlorine atom to obtain new products with various potential applications and properties [13,14].

The glass transition temperature (T_g) is an important intrinsic characteristic that influences the properties of a polymer and its potential applications. Furthermore, polymers with high glass transition temperatures are attractive for industrial polymer science because of strong economic rewards that may arise from their potential applications [15]. In order to raise T_g, the incorporation of rigid or bulky substitutions on the polymer structures has been widely reported [16,17].

Carbazole (Cz), as a heterocyclic aromatic compound containing a dibenzopyrrole system, is produced during coal

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0141-3910/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2006.07.003

gasification and in cigarette smoke. Coal tar produced at high temperature contains an average of 1.5% carbazole. Several thousand tons of carbazole are produced each year from coal tar and crude oil. It is widely used in the synthesis of dyes, pharmaceuticals, and plastics and is a suspected carcinogen [18]. Carbazole is the best-known chromophore that is often used to construct polymers with photoconducting, photorefractive, and hole transporting properties [19,20].

Previous papers about the synthesis and study of the modified properties of various polymers containing highly sterically hindered tris(trimethylsilyl)methyl substituent showed that incorporation of very bulky organosilyl groups into polymer structures leads to an increase in T_g and creates macromolecules with novel architecture that could be used as membranes for gas or fluid separation [21–24].

This present research work describes the synthesis of 4-(*N*-carbazolyl)methyl styrene (CzMS) as a new styrene derivative monomer containing carbazole. Then, CzMS was homopolymerized and copolymerized with some methacrylic and acrylic monomers by the free radical polymerization method. Study of thermal properties of the obtained polymers by DSC curves showed that the incorporation of bulky carbazolyl groups as side chains leads to stiffness of the polymer chains and increase in glass transition temperature.

2. Experimental

2.1. Instruments

Infrared spectra were recorded on a Bruker Spectrometer Tensor 27 FT-IR with KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were run on a Bruker 400 MHz spectrometer at room temperature using $CDCl_3$ as a solvent. Mass spectrum was obtained with a Shimadzu Qp 100X spectrometer at 70 eV. Elemental analysis was carried out with a Heareus CHN-ORAPID instrument. Melting point was determined on a 9100 Electrothermal apparatus. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph fitted with 10^2 and 10^3 Waters Styragel columns. THF was used as elution solvent and polystyrene standards were employed for calibration. Thermal properties were characterized by TGA (TA2050) and DSC (TA2010) at a heating rate 10 °C/min. The T_g's were taken at the midpoints of the heat flow changes.

2.2. Materials

Carbazole (Acros) was purified by crystallization from ethyl alcohol solution before use. Azobisisobutyronitrile initiator (AIBN) was purchased from Merck and purified by crystallization from absolute ethanol. CMS (Aldrich, 90%) was passed through the alumina column and distilled under vacuum (110 °C, 3 mmHg) to remove inhibitors. MMA (Merck), EMA (Merck), EA (Merck) and BA (Merck) were distilled under reduced pressure to remove inhibitors before use. MA (Merck) was distilled at atmospheric pressure and freshly used for polymerization. *N*,*N*-Di-methylformamide (DMF) was dried over anhydrous $MgSO_4$ for 2 days and later with phosphoric anhydride overnight. After drying, DMF was distilled under reduced pressure.

2.3. Synthesis of 4-(N-carbazolyl)methyl styrene

Sodium hydride (1.73 g, 72 mmol) was slowly added to 10.0 g (60 mmol) of carbazole dissolved in 100 ml of DMF at room temperature. After addition of NaH, 11.0 g (72 mmol) of CMS was added to the reaction mixture. The reaction was stirred at 60 °C for 10 h, poured into aqueous NH_4Cl solution and extracted with chloroform. The extract was dried with anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The residue was recrystallized from diethyl ether at −20 °C to give 12.7 g of CzMS (yield: 75%). The solid was dried and stored in glass ampoule under vacuum. M.p. 173 °C; FT-IR (KBr, cm^{-1}): 3060 (C—H aromatic), 2960 (C—H aliphatic), 1630 (C═C vinyl), 1600, 1470 (C═C aromatic), 1320 (C—N); ^{1}H NMR ($CDCl_3$, ppm): 5.24 and 5.65 (d, 2H, ═CH_2), 5.73 (s, 2H, CH_2—N), 6.72 (q, 1H, ═CH), 7.39–8.2 (m, 12H, aryl-H); ^{13}C NMR ($CDCl_3$, ppm): 45.5 (1C, CH_2—N), 112.8 (1C, ═CH_2), 135.6 (1C, ═CH), 110.5, 119.2, 120.1, 122.4, 126.4, 127.5, 136.1, 140.1 (18C, aromatic carbons); *m*/*z* (EI): 284 (M^+), 117 ($[M - Cz]^+$), 91 ($C_6H_5CH_2^+$); Elemental analysis for $C_{21}H_{17}N$ (283) (%) calcd: C 89.0, H 6.0, N 4.9; found: C 88.7, H 6.2, N 5.0.

2.4. Homopolymerization of CzMS

Seven samples of CzMS were polymerized with different times (3–22 h) as follows. A mixture of 2.8 g (10 mmol) of CzMS and 0.033 g (0.2 mmol) of AIBN was dissolved in 10 ml of DMF in a Pyrex glass ampoule. The ampoule was then degassed, sealed under vacuum and shaken in a thermostated water bath at 70 ± 1 °C by a shaker machine for 3–22 h. After this time, the viscous solution was poured into 150 ml of cooled methanol as non-solvent. The white precipitated poly(4-(*N*-carbazolyl)methyl styrene) (PCzMS) was collected, washed with methanol several times and dried in vacuum at room temperature. The yields of polymers were in the range of 29–89%. FT-IR (KBr, cm^{-1}): 3060 (C—H aromatic), 2960 (C—H aliphatic), 1600, 1470 (C═C aromatic), 1330 (C—N); ^{1}H NMR ($CDCl_3$, ppm): 1.4 (2H, CH_2—CH), 1.9 (1H, CH_2—C*H*), 4.9 (2H, CH_2—N), 6.1–8.2 (12H, aryl-H); ^{13}C NMR ($CDCl_3$, ppm): 40 (1C, *C*H_2—CH), 42 (1C, CH_2—*C*H), 46.0 (1C, CH_2—N), 110.5–139.5 (18C, aromatic carbons).

2.5. Copolymerization of CzMS with different monomers: general procedure

Poly(CzMS-*co*-MMA) (**I**), poly(CzMS-*co*-EMA) (**II**), poly(CzMS-*co*-MA) (**III**), poly(CzMS-*co*-EA) (**IV**) and poly(CzMS-*co*-BA) (**V**) were separately prepared as follows. In a Pyrex polymerization tube, 2.8 g (10 mmol) of CzMS and 0.065 g (0.4 mmol) of AIBN were dissolved in 15 ml of