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Polymer 48 (2007) 4301–4304

polymer

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Polymer Communication

Palladium-catalyzed silation of adamantanedi- and triol, leading to adamantane–siloxane alternating polymers with high heat resistance

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Received 7 March 2007; received in revised form 7 May 2007; accepted 18 May 2007
Available online 25 May 2007

Abstract

Palladium-catalyzed dehydrocoupling reactions of 1,3-adamantanediol ($Ad(OH)_2$) with excess amounts of $PhMeSiH_2$ and $PhSiH_3$ gave silated products, $Ad(OSiPhMeH)_2$ and $Ad(OSiPhH_2)_2$, respectively, in good yield. 1,3,5-Adamantantriol ($Ad(OH)_3$) also underwent silation with $PhMeSiH_2$ under the same conditions. When silation of $Ad(OH)_2$ was carried out with 1 equiv of $PhSiH_3$, a polymer consisting of a repeating unit of –O–Ad–OSi(OH)Ph– was obtained. The polymer thus obtained showed high heat resistance and $Td_5 = 420$ °C and $Td_{10} = 512$ °C were noted by its TGA in nitrogen. It was also found that thermal stability of the polymer was improved by using $Ad(OH)_3$ as a comonomer.

Keywords: Adamantane; Hydrosilane; Dehydrocoupling polymerization

1. Introduction

Heat resistant polymers are of current importance, because of their use as functional materials such as, for example, insulating films and encapsulation materials for electronic devices. In this area, polymers with cage frameworks have been actively studied. In particular, an interest has been focused on polymers whose backbone contains adamantane units [1]. However, incorporation of rigid adamantane units into the polymer backbone often suppresses solubility of the resulting polymer. Although introduction of long alkyl or alkoxy side chains to the polymer backbone has been often employed to improve the solubility [1a], this would also affect the polymer thermal properties, decreasing the stability.

On the other hand, siloxane linkage is known as a thermally stable and flexible framework. For instance, thermal degradation of poly(dimethylsiloxane) fluids begins at about 350 °C [2]. It has been demonstrated that the introduction of arylene units into the siloxane backbone improves the thermal stability and a variety of arylene–siloxane alternating polymers have been synthesized so far [2,3]. In the course of our studies concerning the development of silicon based heat resistant polymers [4], we prepared adamantane-containing siloxane polymers. Although polyimides bearing adamantane–siloxane units in the backbone have been prepared, recently [1f], no polymers whose backbone is composed of simple adamantane–siloxane repeating units have been reported. As expected the present adamantane–siloxane polymers exhibited good solubility in organic solvents and showed high heat resistance, in spite of that no aromatic units were incorporated in the polymer backbone.

2. Experimental section

2.1. General

All reactions were carried out in dry nitrogen. Toluene and DMF were dried over sodium and calcium hydride,

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doi:10.1016/j.polymer.2007.05.052

respectively, and were distilled just before use. MS spectra were measured on a Shimadzu QP5050A spectrometer. NMR spectra were measured on a JEOL model LA-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). IR spectra were measured on a Shimadzu IR8700 spectrometer.

2.2. Silation of adamantanedi- and triol

A mixture of adamantanediol (Ad(OH)$_2$) (0.501 g, 2.98 mmol), methylphenylsilane (1.11 g, 9.05 mmol), and PdCl$_2$ (4.9 mg, 0.028 mmol), in toluene (5 mL) was refluxed for 24 h. After filtration, the solvent was evaporated and the residue was distilled under reduced pressure to give **1a** (0.934 g, 2.27 mmol, 77% yield) (Scheme 1): GC–MS *m/z* 408 (M$^+$), 331 (M$^+$ − Ph), 287 (M$^+$ − SiHMePh), 271 (M$^+$ − OSiHMePh); ^{1}H NMR (δ in CDCl$_3$) 0.40 (d, $J = 2.90$ Hz, 6H, SiCH$_3$), 5.15 (q, 2H, $J = 2.90$ Hz, SiH), 1.40–2.20 (m, 14H, Ad, 7.35–7.42 (m, 6H, Ph), 7.58–7.60 (m, 4H, Ph); ^{13}C NMR (δ in CDCl$_3$) −0.33 (SiCH$_3$), 31.27, 34.58, 43.95, 44.00, 52.94, 74.10 (Ad), 127.82, 129.69, 133.66 (Ph CH), 137.77 (Ph ipso C). Anal. calcd for $C_{24}H_{32}O_2Si_2$: C, 70.53; H, 7.89. Found: C, 70.23; H, 8.19.

Other silation of Ad(OH)$_2$ and adamantanetriol (Ad(OH)$_3$) was carried out in a similar fashion to that above. Data for **1b**: 70% yield; ^{1}H NMR (δ in CDCl$_3$) 1.47–2.26 (m, 14H, Ad), 5.06 (s, SiH), 7.36–7.43 (m, 6H, Ph), 7.58–7.65 (m, 4H, Ph); ^{13}C NMR (δ in CDCl$_3$) 31.27, 34.48, 43.45, 51.97, 74.42 (Ad), 128.00, 130.24, 134.38 (Ph CH), 135.60 (Ph ipso C). Data for **2a**: 83% yield; ^{1}H NMR (δ in CDCl$_3$) 0.38 (d, $J = 2.9$ Hz, 9H, SiCH$_3$), 1.54–2.21 (m, 13H, Ad), 5.10 (q, 3H, $J = 2.90$, SiH), 7.34–7.42 (m, 9H, Ph), 7.55–7.57 (m, 6H, Ph); ^{13}C NMR (δ in CDCl$_3$), −0.49 (SiCH$_3$), 29.54, 42.67, 51.86, 74.35, (Ad), 127.88, 129.81, 133.66 (Ph CH), 137.37 (Ph ipso C). Anal. calcd for $C_{32}H_{42}O_3Si_3$: C, 68.76; H, 7.57. Found: C, 69.02; H, 7.51.

2.3. Polymer synthesis

A mixture of Ad(OH)$_2$ (0.448 g, 2.66 mmol), PhSiH$_3$ (0.288 g, 2.66 mmol), and PdCl$_2$ (9.1 mg, 0.051 mmol) in DMF (15 mL) was stirred at 140 °C for 48 h. The resulting black precipitates were filtered and ether and water (20 mL each) were added to the filtrate to precipitate polymeric products. The colorless solids thus precipitated were collected and reprecipitated from THF-hexane to give polymer **3** (0.121 g, 17% yield) (Scheme 2): $M_w = 32{,}000$, $M_w/M_n = 1.7$; mp > 300 °C; ^{1}H NMR (δ in CDCl$_3$) 1.19–3.15 (br m, 14H adamantane H), 6.95–8.00 (br m, 5H, phenyl ring H), hydroxy proton signal may overlap with that of the adamantane unit; ^{13}C NMR (δ in CDCl$_3$) 30.42–32.26 (br m, Ad), 34.54, 34.79 (Ad), 42.92–44.48 (br m, Ad), 74.35–74.61 (br m, Ad), 127.20–127.91 (br m, Ph), 133.90–134.75 (br m, Ph); ^{29}Si NMR (δ in CDCl$_3$) −0.79; IR (KBr) 1067, 1130 (SiO), 3390 (br, OH) cm^{-1}. The low molecular weight fraction was separated by reprecipitation of the ether-soluble part, from THF-hexane as a colorless solid: $M_w = 3400$, $M_w/M_n = 1.2$; mp 118–123 °C; ^{1}H NMR (δ in CDCl$_3$) 0.87–2.49 (br m, 14H, Ad), 6.55–7.98 (br m, 5H, Ph); ^{13}C NMR (δ in CDCl$_3$) 31.20, 31.21, 21.28, 34.53, 34.69, 43.84, 43.98, 44.23, 44.37, 52.82, 53.30, 53.48, 70.45, 70.51, 74.37, 74.68 (Ad), 126.25–128.00 (br m, Ph), 129.20–131.11, (br m, Ph), 133.75–135.42 (br m, Ph); IR (in KBr) 1052, 1132 (SiO), 3405 (br, OH) cm^{-1}.

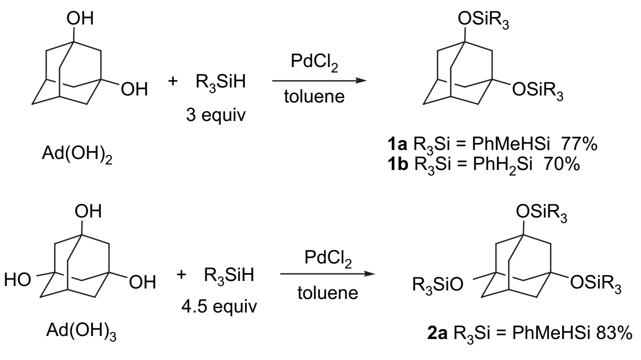
Other polymers shown in Scheme 3 were obtained in a similar fashion to that of the above. Data for **4a**: $M_w = 52{,}000$, $M_w/M_n = 2.7$; mp > 300 °C; ^{1}H NMR (δ in CDCl$_3$) 0.30–3.50 (br m, 14H, Ad), 7.29 (br s, 3H, Ph), 7.61 (br s, 2H, Ph); ^{13}C NMR (δ in CDCl$_3$) 31.3, 34.7, 44.2, 53.3, 74.4 (br m, Ad), 127.4, 129.6, 134.5 (br m, Ph); IR (in NaCl) 1065, 1126 (SiO), 3371 (br, OH) cm^{-1}. Spectral data obtained for **4b** and **4c** are essentially the same as those for **4a**.

3. Results and discussion

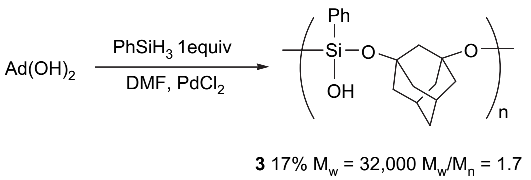
3.1. Silation of Ad(OH)$_2$ and Ad(OH)$_3$

Recently, we have demonstrated that PdCl$_2$-catalyzed reactions of di- and trihydrosilanes with alcohols afford the corresponding dehydrocoupling products in good yield [5]. These reactions proceed selectively, producing partially or wholly substituted alkoxyhydrosilanes depending on the reaction stoichiometry. In this system, PdCl$_2$ is first reduced by hydrosilanes to fine Pd(0) powder, which catalyzes the reactions via the formation of silyl radical intermediates.

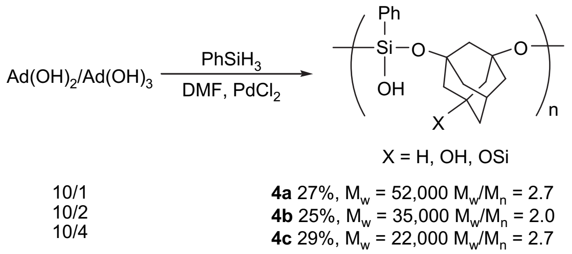
First, we examined model reactions to know if the PdCl$_2$-catalyzed system can be applied to silation of adamantanedi- and triol (Ad(OH)$_2$ and Ad(OH)$_3$). When Ad(OH)$_2$ or Ad(OH)$_3$ was heated with excess hydrosilanes in toluene at the reflux temperature in the presence of PdCl$_2$ as the catalyst and the resulting organic products were distilled under reduced pressure, silated products **1a**, **b** and **2a** were obtained in good



Scheme 1.



Scheme 2.



Scheme 3.

isolated yield, as shown in Scheme 1. No other volatile products were detected by GC–MS analysis of the reaction mixtures.

3.2. Polymer synthesis

For polymerization, $Ad(OH)_2$ was treated with 1 equiv of $PhSiH_3$ in DMF at 140 °C for 48 h. Reprecipitation of the resulting organic products from THF–hexane gave polymer **3** as the colorless solids (Scheme 2). Molecular weight of the polymer was determined to be $M_w = 32{,}000$ ($M_w/M_n = 1.7$) by GPC, relative to polystyrene standards. As expected polymer **3** was soluble in common organic solvents with adequate polarity, such as chloroform, THF, and DMF, but barely soluble in saturated and aromatic hydrocarbons, diethyl ether, and alcohols. We also attempted similar polymerization of $Ad(OH)_2$ with $PhMeSiH_2$ under the same conditions. However, in this reaction, only a low molecular weight oligomer ($M_w = 2100$, $M_w/M_n = 1.1$) was obtained in 66% yield. This is in contrast to similar cross-dehydrocoupling of bis(hydrodimethylsilyl) compounds with diols, reported by Kawakami et al. They have reported that these reactions were readily catalyzed by $Pd_2(dba)_3$, Pd/C, and $RhCl(PPh_3)_3$ to give the corresponding polymers with moderate molecular weights in high yield [3b,6].

The structure of **3** was verified by spectrometric analysis. ^1H and ^{13}C NMR spectra of **3** showed slightly broad but strong signals, which were assignable to phenyl and adamantanediyl signals by comparison with those of **1a** and **1b**. No other major signals were observed in these spectra. ^1H NMR spectrum of **3** showed no signals due to Si–H bonds and its ^{29}Si NMR spectrum showed only one signal at −0.79 ppm, presumably due to phenyltrioxy silicon atoms. In its IR spectrum, no bands ascribed to the Si–H vibration (about 2100 cm^{-1}) were observed, but a strong broad band of OH vibration appeared around 3400 cm^{-1}. On the other hand, the rather small value of polydispersity ($M_w/M_n = 1.7$) determined by GPC analysis of the polymer as well as high solubility of **3** seemed to indicate that the polymer did not possess a considerable amount of cross-linked units. On the basis of these considerations, we concluded that one of the Si–H bonds in $PhSiH_3$ was converted to an Si–OH bond by hydrolysis during purification of the polymer, as shown in Scheme 2.

Thermal properties of polymer **3** were examined by thermogravimetric analysis (TGA). Temperatures of 5% and 10% weight loss (Td_5 and Td_{10}), and total weight loss at 800 °C in nitrogen and in air were noted as listed in Table 1. With respect to Td_{10}, polymer **3** was found to be more thermally stable than poly(adamantanediyl)s (Td_{10} in nitrogen = 486 °C) [1a]. When compared with dimethylsiloxane high polymer [7], polymer **3** showed a little lower Td_5, but a slightly higher Td_{10}, with comparable thermal stability. A smaller molecular weight fraction ($M_w = 3400$, $M_w/M_n = 1.2$, 33% yield) was also separated from the reaction mixture of $Ad(OH)_2$ and $PhSiH_3$, but its TGA showed much inferior heat resistance with lower Td_5 and Td_{10} by about 100 °C than those of polymer **3**.

Table 1
Thermal properties of polymers containing adamantane units[a]

Polymer	TGA in N_2			TGA in air		
	Td_5/°C	Td_{10}/°C	wt loss/%	Td_5/°C	Td_{10}/°C	wt loss/%
3	420	512	46	376	407	76
4a	453	514	44	403	428	68
4b	460	520	39	383	406	68
4c	473	522	41	397	433	61

[a] TGA was carried out at a rate of 10 °C/min. Td_5 and Td_{10} are temperatures resulting in 5% and 10% weight loss from the initial weight, respectively. Weight loss at 800 °C is given on the basis of the initial weight of the polymer sample.

Using $Ad(OH)_3$ as a comonomer in this polymerization improved heat resistance of the resulting polymers (see Scheme 3, Table 1). The Td_5 and Td_{10} values were elevated on increasing the monomer ratio of $Ad(OH)_3/Ad(OH)_2$ taken as monomers. ^1H and ^{13}C NMR spectra of polymers **4a–c** showed broader signals than those for polymer **3**. Their polydispersities were determined to be considerably higher than that for **3** by GPC. These results were indicative of the fact that polymers **4a–c** had cross-linked units to an extent, which would be responsible for the superior heat resistance of **4a–c**, relative to **3**. As can be seen in Table 1, the total weight loss at 800 °C was decreased by employing $Ad(OH)_3$ as the comonomer with the lowest value of about 38% based on the initial weight for **4b**. Although the reason why polymer **4c** showed higher weight loss at 800 °C than **4b** is still unclear, the lower molecular weight of **4c** possibly affected the weight loss. Incorporation of cross-linked units into the polymer backbone would sterically suppress the polymer reactivity to lower the molecular weights. Polymers **4a–c** showed similar solubility to that of **3**.

In conclusion, we prepared polymers with adamantane–siloxane alternating units in the backbone by simple one step synthesis and found that these polymers showed good heat resistance and solubility in organic solvents. Introduction of cross-linked units improved the heat resistance, without losing the polymer solubility, and the Td_5 and Td_{10} reached 473 °C and 522 °C, respectively. Although the thermal degradation mechanism is still unclear, the adamantane–siloxane system is of high potential for the core structure of thermally stable materials.

Acknowledgement

This work was supported by a Grant-in Aid for Scientific Research (no. 17550105) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, to which our thanks are due.

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