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Cyclopolymerization
XXXIII. Radical polymerizations and copolymerizations of 1,6-dienes with 2-phenylallyl group and thermal properties of polymers derived therefrom

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Abstract

Radical polymerizations of α-allyloxymethylstyrene (**1**) and copolymerizations of α-(2-phenylallyloxy)methylstyrene (**2**) were undertaken to acquire comprehensive understanding on polymerization behavior of these dienes and to get polymers with high thermal stability and high glass transition temperature (T_g). One of the monofunctional counterparts of **1** is a derivative of α-methylstyrene, the ceiling temperature of which is low, and the other is an allyl compound that is well-known for the low homopolymerization tendency. This means that the intermolecular propagation reactions leading to pendant uncyclized units are suppressed during the polymerization of **1** to yield highly cyclized polymers. In fact, the degree of cyclization of poly(**1**) obtained at 140 °C attained the value 92%. Structural studies revealed that repeat cyclic units of poly(**1**) consist exclusively of five-membered rings. Poly(**1**) was found to be stable up to 300 °C, but its T_g values were detected at around 100 °C. They are considerably lower than the targeted values which should lie between 180 and 220 °C. An additional drawback of poly(**1**) is its low molecular weight probably due to a degradative chain transfer. For this reason, copolymerizations of **2** with **1** and with styrene were also carried out to seek for the possibility to control the thermal properties precisely. Monomer **2** was chosen, since it has been reported in our previous work that it yields polymers with thermal stability up to 300 °C and T_g higher than 250 °C. Copolymerization of **2** with styrene afforded polymers with desired thermal properties and high molecular weight.

Keywords: Radical cyclopolymerization; High glass transition temperature; Thermally stable polymer; 1,6-Diene

1. Introduction

Polymerization of α-allyloxymethylstyrene (**1**) and copolymerization of α-(2-phenylallyloxy)methylstyrene (**2**) (Scheme 1) were undertaken to obtain comprehensive understanding on polymerization behavior of these

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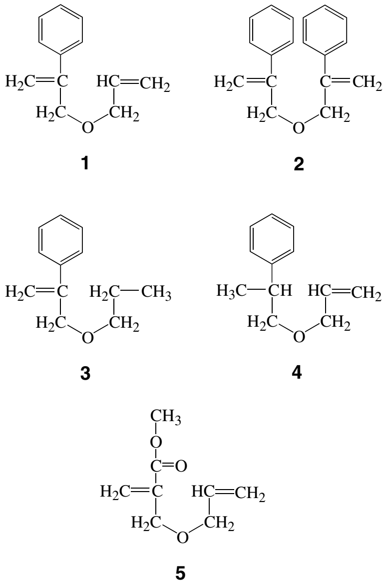

Scheme 1. Structural formulae of **1**–**5**.

dienes and to get polymers with high thermal stability and a high glass transition temperature (T_g). This is because the recent development in advanced technology is in need of materials with such properties in various aspects of application, for example, as a material for hard disks. Polymers with high degrees of cyclization derived from 1,6-dienes have excellent thermal properties as compared to the conventional linear vinyl polymers. For this reason monomer **1** was designed, since formation of highly cyclized polymers is expected therefrom judging from the following considerations. α-Propoxymethylstyrene (**3**), one of the monofunctional counterparts of **1**, is a derivative of α-methylstyrene, the ceiling temperature of which is low, and 2-phenylpropyl allyl ether (**4**) (Scheme 1), the other monofunctional counterparts of **1**, is the allyl compound that is well-known for low homopolymerization tendency. This means that C═C double bonds of **1** have low homopolymerizability, when they exist as a monoene compound. Accordingly, the intermolecular propagation reactions leading to pendant uncyclized units are hard to occur during its polymerization and formation of highly cyclized polymers is expected therefrom [1]. In our previous work, synthesis and polymerizations of **2** were undertaken to achieve the purpose mentioned above [2], since the monoene counterpart of **2** is a derivative of α-methylstyrene. In fact, highly cyclized polymers were obtained which consist mainly of 6-membered rings and have thermal stability up to 300 °C and T_g higher than 250 °C. However, the T_g values of poly(**2**) were much higher than the targeted values which should lie between 180 and 220 °C for easy processing. Repeat cyclic units attached with two bulky phenyl groups through the main chain endow poly(**2**) with high rigidity, which makes its T_g too high. This is the reason why **1** with one phenyl group of **2** substituted by a hydrogen atom was designed and its polymerization behavior was investigated. Along with these studies, copolymerizations of **2** with **1** and with styrene were also undertaken to gain fundamental information on their cyclocopolymerizabilities and to seek for the possibility to obtain polymers with precisely controlled thermal properties.

2. Experimental

2.1. Materials

Monomer **1** was prepared according to the procedure reported for the synthesis of similar compounds [3]. In a 1l round bottomed flask equipped with a reflux condenser and a thermometer, 26.4 g (0.2 mol) of α-hydroxymethylstyrene (HMS), 232.7 g (1.9 mol) of allylbromide (AB), and 332 g of 12% aqueous NaOH solution were placed. The reaction mixture was refluxed for 53 h under the presence of 4.62 g of tetra-*n*-butylammonium bromide (TBA). After cooling the reaction mixture to room temperature, water layer was washed with ethyl ether. Combined organic layer and ethyl ether were dried over anhydrous sodium sulfate overnight. After removing volatile materials by evaporation, the residual oil was purified by column chromatography on silica gel (Cyclohexane:Chloroform = 1:1) to give **1** with a yield of 68%. The boiling point of **1** is 75 °C/1.0 mmHg. *Anal.* Calcd for $C_{12}H_{14}O$ (**1**): C, 82.72%; H, 8.10%. Found: C, 82.59%; H, 8.11%. Chemical shifts of the characteristic absorption peaks of ^1H and ^{13}C NMR spectra of **1** are as follow. ^1H NMR: $\delta = 7.46–7.19$ (m, 5H, $–C_6\,H_5$), 5.96–5.88 (m, 1H, $–\mathit{H}C{=}CH_2$), 5.51, 5.34 (s, 2H, $\mathit{H}_2C{=}C–C_6H_5$), 5.27, 5.17 (d, 2H, $–CH{=}C\mathit{H}_2$), 4.38 (s, 2H, $C_6H_5–C–C\mathit{H}_2–O–$), 4.02 (d, 2H, $–O–C\mathit{H}_2–CH{=}CH_2$) ppm, ^{13}C NMR: $\delta = 144.3$ ($CH_2{=}\mathit{C}–C_6H_5$), 134.7 ($–\mathit{C}H{=}CH_2$), 138.9, 128.3, 127.7, 126.0 ($–\mathit{C}_6H_5$), 117.0 ($–CH{=}\mathit{C}H_2$), 114.2 ($\mathit{C}H_2{=}C–C_6H_5$), 71.9 ($C_6H_5–C–\mathit{C}H_2–O–$), 71.0 ($CH_2{=}CH–\mathit{C}H_2–O–$) ppm.

The reported procedures were employed for the syntheses of HMS [4]. Benzene was washed successively with concentrated sulfuric acid, water, 5% aqueous sodium hydroxide, and finally water and subsequently refluxed over sodium metal and distilled. Commercial TBA and cumene hydroperoxide were used as-received. Commercial azobis(isobutyronitrile) (AIBN) was recrystallized from ethyl alcohol. All common solvents were purified by usual methods.

2.2. Polymerization

Polymerizations were performed in sealed tubes. A given amount of monomer and initiator were placed in