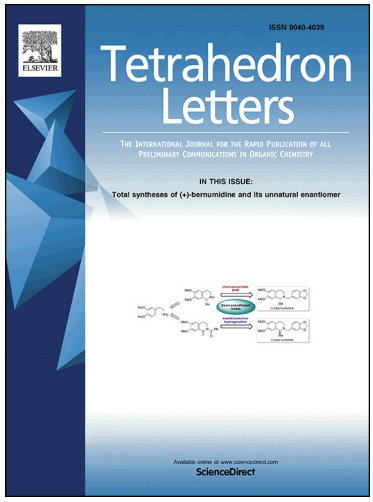

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Co-cross-linking of Bio-based Multi-functional Epoxide and Bisphenol A Diglycidyl Ether with 2-Ethyl-4-methylimidazole

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ABSTRACT

A co-cross-linking reaction of bio-based multi-functional epoxides (**1**) derived from limonene oxide and bisphenol A diglycidyl ether (BPADE) in the presence of 2-ethyl-4-methylimidazole (EMI) as a cross-linker afforded the corresponding network copolymers (**2**) having the 10 % thermal decomposition temperature (T_{d10}) of 294.4 °C at maximum. Adhesive strength induced by **1**, especially tetra-functional epoxide, and BPADE exhibited remarkably higher than that by BPADE alone.

Petroleum is one of the most important non-renewable resources. Chemical industrial products such as plastics and polymers are mainly derived from petroleum. Use of renewable resources such as biomass for synthesizing polymeric materials is a reasonable way in order to build a sustainable society. One of the promising candidates of biomass is citrus peel oil.[1)] Major component in citrus peel oil is limonene,[2),3),4)] oxidation of which affords limonene oxide (LO). Very recently, we have reported in earlier work a synthesis of multi-functional epoxides (**1**) derived from LO composed of a *cis*- and *trans*-isomer mixture, which allowed for a cross-linking reaction with branched polyethyleneimine (BPEI) as a cross-linker.[5)] The corresponding network polymers have the 10 % thermal decomposition temperature (T_{d10}) of 140.7–243.2 °C. So far, there is nothing but BPEI to proceed the cross-linking reaction of **1** to give the corresponding network polymer. In this study, we tried to find out another way to afford the bio-based cross-linked network from **1** having high thermal resistance and mechanical property.

1 was synthesized according to our previous report.[5)] Co-cross-linking of **1** and bisphenol A diglycidyl ether (BPADE) was performed with 2-ethyl-4-methylimidazole (EMI) as a cross-linker. EMI is widely used as the traditional cross-linker for epoxy resin, catalytic amount of which affords the network polymers with excellent chemical and thermal resistance, and physical property.[6),7),8)] No network polymer was obtained by the cross-linking reaction of **1** alone by EMI as shown in Table 1, despite of number of epoxy groups; however, we found that the cross-linked copolymerization of **1** and BPADE successfully proceeded with EMI (5 mol% to total of epoxy moiety) at 100 °C for 24 h as shown in Scheme 1. We first examined the co-cross-linking of bis-functional epoxide **1a** and BPADE with initial feed of [**1a**]$_0$:[BPADE]$_0$=71:29 (wt:wt), giving the network copolymer (**2a**) composed of 28 % of **1**a in 41 % yield. Degree of incorporation of **1** into **2** was calculated based on the ratio of the weight percentage of sulfur in **2** estimated by elemental analysis and the weight percentage of sulfur in **1** (Table 1). In order to increase of composition ratio of **1** to **2**, tetra-functional epoxide **1b** was employed as the bio-based monomer. The co-cross-linking of **1b** and BPADE with feed ratio of [**1b**]$_0$:[BPADE]$_0$=50:50 (wt:wt) resulted in the synthesis of **2b** having degree of incorporation of 53 % in 56 % yield. The yield of copolymer increased with an increase of amount of EMI, while no significant change in composition ratio was observed (Table 1). Degree of biomass (DB) values calculated from the composition of **2b** ranged from 27 % to 31 %. The Japan BioPlastics Association (JBPA) defines that biomass-derived plastics have biomass content more than 25 wt%.[5),9),10),11)] Based on this definition, **2b** was classified as the biomass-derived polymer in all cases. Solubility of **2** was found to be insoluble in any solvent such as acetone, chloroform, tetrahydrofuran, *N*-methyl-2-pyrrolidone, and water, indicating the successful formation of a cross-linked network.

Thermal resistance was investigated by thermogravimetric (TG) analysis. Figure 1 shows representative examples of TG curves of **2**. The thermal behavior of **2a** and **2b** at temperature lower than around 400 °C seems different from that of **2** derived from BPADE only, supporting the incorporation of **1a** and **1b** into the network copolymers. The T_{d10} values of **2a** and **2b** were

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