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THE INFLUENCE OF CROSS-LINKING AGENTS ON RING-OPENING METATHESIS POLYMERIZED THERMOSETS

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The addition of suitable cross-linking agents with norbornene-based monomers has significant effects on the thermal properties of the resulting polymers formed by olefin metathesis. Ethylidene norbornene (ENB) and *endo*-dicyclopentadiene (*endo*-DCPD) were mixed separately with various loadings of three different cross-linking agents and then polymerized with the addition of Grubbs' catalyst. The polymerization kinetics and resulting glass transition temperature (T_g) of the systems were evaluated by differential scanning calorimetry (DSC).

The addition of the first cross-linking agent, norbornadiene (CL-1), to both *endo*-DCPD and ENB resulted in decreasing glass transition temperatures with increasing concentrations. In contrast, the addition of the other two cross-linking agents (CL-2 and CL-3), which were both custom synthesized bifunctional norbornyl systems, to both *endo*-DCPD and ENB resulted in a monotonic increases in T_g with cross-linker concentration. By tailoring the loading of these custom cross-linking agents, the properties of these polymer systems can be controlled for various applications, including self-healing composites.

Keywords: *cross-linking agent, dicyclopentadiene, glass transition temperature, ROMP*

Introduction

Transition-metal-catalyzed ring-opening metathesis polymerization (ROMP) is a powerful reaction for the synthesis of various polymers from cyclic alkenes [1]. In the last decade, significant advances have been made in ROMP initiators and resulting homopolymers and copolymers. Ruthenium-based catalysts developed by Grubbs [2] exhibit remarkable tolerance toward oxygen, moisture and numerous functionalities. With the advances in catalysts for ROMP reactions, applications of ROMP have been widened to various fields. For structural applications, ROMP is often used to polymerize low viscosity monomers in reaction injection molding (RIM) techniques. ROMP was also used in recently developed self-healing composite materials, where self-healing is accomplished by incorporating a microencapsulated norbornene-based healing agent and a catalytic chemical trigger within a polymer matrix [3]. In this application, as in RIM, the addition of multifunctional cross-linking agents to the ROMP monomers affects the cross-linking density and thermo-mechanical properties of the resulting polymer.

Norbornene-based monomers (Fig. 1), *endo*-dicyclopentadiene (DCPD) 1 and *exo*-DCPD 2 polymerize, with the addition of ruthenium-based Grubbs catalyst, to form cross-linked polymers of high toughness. Recent studies showed that *exo*-DCPD is more reactive than *endo*-DCPD for ROMP primarily for steric reasons [4]. Only *endo*-DCPD is commercially available and it is necessary to synthesize *exo*-DCPD from *endo*-DCPD. Another ROMP monomer for structural and self-healing applications is 5-ethylidene-2-norbornene (ENB) 3, which has higher ROMP reactivity but polymerizes into a linear polymer. However, ENB can be blended with DCPD or added with cross-linking agents to form a cross-linked network. The addition of suitable cross-linking agents with any of these monomers has significant effects on the thermal properties of the resulting polymer.

Several norbornene-based ROMP cross-linking agents (CL-1 to CL-3) with varying degrees of complexity (shown in Fig. 1) were purchased or synthesized in our laboratory to meet different application requirements [5–7]. By adding the cross-

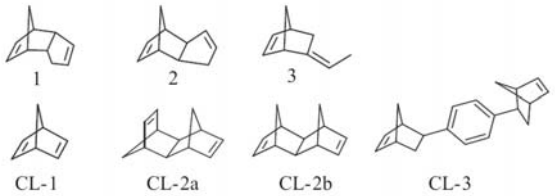

Fig. 1 ROMP monomers and cross-linking agents

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linking agents at varying concentrations to the ROMP monomers, the cross-linking density of the polymerized system is changed, resulting in controlled properties for various applications, including self-healing composites. In addition to the tailored cross-linking density that may be obtained by adding cross-linking agents to the monomers, the cross-linking agents may also accelerate the ROMP reaction, especially when mixed with the sterically hindered *endo*-DCPD monomer.

The ROMP polymerization, initiated by bis(tricyclohexylphosphine)benzilidene ruthenium(IV) dichloride (Grubbs' 1st generation catalyst), of both DCPD and ENB are highly exothermic because of the relief of ring strain energy [8]. The first step of this process involves dissociation of a phosphine ligand from the precatalyst. Then, the resulting 14-electron complex undergoes a [2+2] cycloaddition with monomer to give a metallocyclobutane intermediate 4, which rapidly undergoes a [2+2] cycloreversion to produce the ring-opened product 5. Intermediate 5 contains a catalytically active Ru-alkylidene, and undergoes further chain growth reactions until the monomer is completely consumed. For DCPD, the remaining double bond may be polymerized in a similar way to form a cross-linked poly-DCPD network. Figure 2 illustrates the ROMP mechanism for the *endo*-DCPD/CL-3 system. With cross-linking agent CL-3, a highly cross-linked poly-DCPD network is formed.

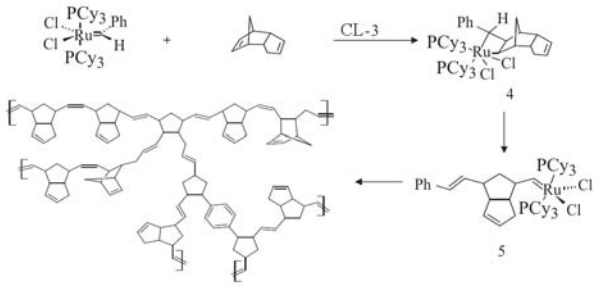

Fig. 2 ROMP mechanism for *endo*-DCPD system containing cross-linking agent (CL-3)

In this paper, we report on the use of differential scanning calorimetry (DSC) to evaluate the polymerization of *endo*-DCPD, *exo*-DCPD and ENB. Three kinds of cross-linking agents, CL-1, 2 and 3, were mixed with *endo*-DCPD and ENB separately, and then polymerized. The glass transition temperatures (T_g) of cured samples were investigated in detail by DSC.

Experimental

All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. All reactions were carried out in oven-dried glassware under a dry nitrogen atmosphere at ambient temperature unless otherwise stated. Flash column chromatography was carried out on MP silica gel 60, grade 32–63 μm.

Preparation of exo-dicyclopentadiene

Exo-DCPD was synthesized from the endo-isomer by a slight modification of literature methods [9]. Hydrobromic acid aqueous solution (48%, 172.8 g) was added to fresh *endo*-dicyclopentadiene (70.2 g, 0.53 mol) distillate by addition funnel. The reaction was carried out at 75°C for 12 h and was cooled to room temperature. After the addition of water (100 mL), 5% sodium bicarbonate solution was added to neutralize the reaction mixture. Subsequently, the mixture was extracted with Et_2O (3·200 mL). The combined extract was dried with anhydrous sodium sulfate. After removal of Et_2O by rotavapor, reduced pressure distillation gave a colorless liquid, hydrogen bromine adduct (b.p. 86~88°C/0.1 mmHg). A solution (4.82 mol L^{-1}) containing potassium hydroxide (63.1 g) in 95% ethanol (233.5 mL) was added to the hydrogen bromine adduct (79.4 g, 0.37 mol) by addition funnel. The mixture was heated under refluxing for 24 h. After the addition of water (100 mL), the mixture was extracted with Et_2O (3·200 mL). The combined extract was dried with anhydrous sodium sulfate. After removal of Et_2O by rotavapor, reduced pressure distillation gave the dehydrohalogenation product contained 10% *endo*-DCPD. The dehydrohalogenation product was re-distilled at 190°C; *endo*-DCPD was decomposed and distilled out. Reduced pressure distillation of residue gave *exo*-DCPD (b.p. 60°C/0.2 mmHg, 31.7 g, overall yield 45.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (m, 2H), 5.75 (m, 1H), 5.54 (m, 1H), 2.66 (s, 1H), 2.57 (s, 2H), 2.50 (m, 1H), 2.21 (m, 1H), 1.89 (m, 1H), 1.48 (m, 1H), 1.31 (m, 1H).

Preparation of CL-2 and CL-3

Norbornene-based cross-linking agents (CL-2 and 3) were synthesized by following reported methods [7, 10].

Cross-linking agent CL-2, the mixture of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*,-*endo*-dimethanonaphthalene (CL-2a) and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo*,-*endo*-dimethanonaphthalene (CL-2b), was prepared by adding bicyclo[2.2.1]hepta-2,5-diene (8.6 g, 93.3 mmol) and hydroquinone (13 mg,

0.12 mmol) to *endo*-dicyclopentadiene (6.2 g, 46.9 mmol). The reaction was carried out in hard-glass pressure vessel at 190°C for 18 h. The resulting mixture was subjected to reduced pressure fractional distillation and gave cross-linking agent CL-2 (7.8 g 52.9%), which is the mixture of *exo*-, *endo*-isomer CL-2a (83%) and *endo*-, *endo*-isomer CL-2b. ^{1}H NMR for CL-2a (300 MHz, $CDCl_3$) δ 6.20 (m, 2H), 6.03 (m, 2H), 2.67 (m, 2H), 2.60 (m, 1H), 2.47 (m, 2H), 2.19 (m, 2H), 1.62 (m, 1H), 1.49 (m, 1H), 0.96 (m, 1H). ^{1}H NMR for CL-2b (300 MHz, $CDCl_3$) δ 5.30 (m, 4H), 2.70 (m, 2H), 2.59 (m, 4H), 1.48 (m, 4H).

Cross-linking agent CL-3, 1,4-di-(*exo*-bicyclo[2.2.1]hept-5-en-2-yl)benzene, was prepared by first adding bicyclo[2.2.1]hepta-2,5-diene (5.00 g, 5.43 mmol), DMF (5 mL), 1,4-diiodobenzene (1.40 g, 4.22 mmol) and piperidine (2.2 mL, 22.22 mmol) and bubbling with dry nitrogen. Bis(triphenylphosphine)palladium(II) acetate (0.324 g, 0.43 mmol) was added to the mixture and bubbled with nitrogen until it was completely dissolved. The mixture was cooled to 0°C. Subsequently, formic acid (0.86 mL, 22.79 mmol) was added slowly. On completion of the addition of formic acid, the temperature was warmed up to room temperature over 2 h. The reaction mixture was heated to 60°C for 4 h and was cooled to room temperature. After the addition of water (100 mL), the mixture was extracted with Et_2O (3·100 mL). The combined extracts were dried with anhydrous sodium sulfate and concentrated by rotavapor. Chromatography (hexanes) of the residue gave cross-linking agent CL-3 (0.866 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 4H), 6.26 (m, 2H), 6.16 (m, 2H), 2.96 (s, 2H), 2.88 (s, 2H), 2.70 (m, 2H), 1.57 (m, 6H), 1.42 (m, 2H).

Differential scanning calorimetry

Bis(tricyclohexylphosphine)benzilidene ruthenium(IV) dichloride (Grubbs' 1st generation catalyst) was purchased from Sigma-Aldrich as a purple powder. First, 10 mg Grubbs' catalyst was dissolved in 10 mL of methylene chloride. The required amount of catalyst solution (to obtain a 2.0 mg mL^{-1} catalyst concentration in samples) was added to vials using a syringe. Methylene chloride was removed by dry nitrogen flow and the catalyst formed much smaller, more soluble crystals than the crystalline form of the 'as-received' catalyst [11]. Then, monomer was added to the vial and the vial was vigorously mixed for less than 10 s to dissolve the catalyst powder, forming a homogeneous solution. Because of high reactivity, ENB monomer was mixed with catalyst at 0°C or in a low temperature dry ice bath (water/ethanol=50/50, volume ratio). The solution was added dropwise into liquid nitrogen to create small frozen droplets of catalyzed monomer. Finally, the small frozen beads of catalyzed monomer were placed into aluminum DSC sample pans and loaded into the DSC chamber at a standby temperature of –50°C.

To investigate how the concentrations of cross-linking agents influence the cure kinetics and resulting glass transition relaxation properties of the systems, two series of samples were prepared each containing the cross-linking agents mixed with either *endo*-DCPD or ENB. For each series, cross-linking agents CL-1, CL-2 and CL-3 were added at various loading. Isothermally cured samples were prepared in order to measure the final glass transition temperature by first dissolving cross-linking agents into *endo*-DCPD or ENB at varying monomer/cross-linking agent ratio. This solution was then added to a vial containing the required amount of re-crystallized catalyst. After the catalyst was completely dissolved, the catalyzed monomer/ cross-linking agent solutions were dropped into DSC sample pans and fully cured isothermally in a programmable oven at a preset temperature of 70°C for 1 h, then 170°C for 30 min. Finally, the sample pans containing the fully cured samples were loaded into the DSC chamber at a standby temperature of 25°C.

The concentration of cross-linking agents in the mixtures ranged from 2.6 to 24.8 mass% while the catalyst concentration was fixed at 2.0 mg mL^{-1} for all samples. DSC measurements were performed with a Perkin Elmer Pyris 1 DSC system. The DSC cell was swept by a constant flow of nitrogen at 20 mL min^{-1}. Tests were performed in a dynamic mode at heating rates of 10°C min^{-1} (unless otherwise stated) over a temperature range of –50–200°C for evaluation of polymerization of monomers and 25–200°C for measurement of glass transition temperature.

Results and discussion

Typical DSC scans for the three ROMP monomers are shown in Fig. 3. The polymerization of *endo*-DCPD, *exo*-DCPD and ENB are highly exothermic because of the relief of ring strain energy. The location and form of the exothermic peaks indicate that ENB has the highest reaction activity among these three norbornene-based monomers [12, 13]. Additionally, because of the low melting point (–80°C), polymerization of ENB was started as low as –20°C. Therefore, it is necessary to prepare samples contained ENB monomer at very low temperature.

Evaluations of polymerization were performed in a dynamic mode at various heating rates by DSC.

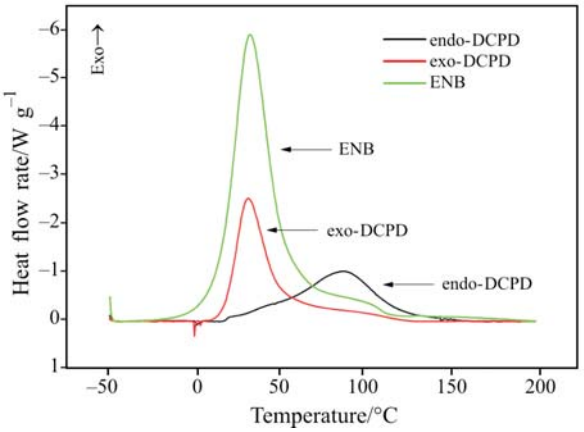

Fig. 3 Typical DSC dynamic scans at 10°C min^{-1} (catalyst concentration: 2 mg mL^{-1})

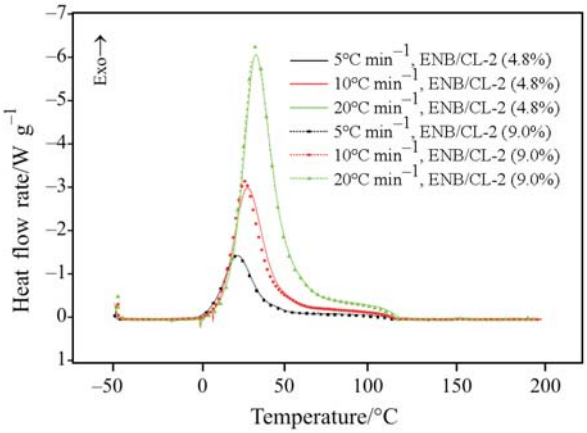

Fig. 4 DSC dynamic scans at different heating rates for the ENB samples with two different concentrations of CL-2 (catalyst concentration: 2 mg mL^{-1})

T_g measurements of fully cured samples were performed at a fixed heating rate of 10°C min^{-1}. Figure 4 shows DSC scans at different heating rates for the polymerization of ENB/CL-2 systems. There was no difference between thermograms from ENB with 4.8% CL-2 (solid line) and ENB with 9.0% CL-2 (dotted lines with symbols). This indicates that extra crosslinking agents added to the systems do not have a significant effect on cure kinetics for ENB systems (though the same cannot be said for the sterically inhibited *endo*-DCPD systems). But, as expected, the glass transition temperature of the resulting networks increases with increasing loadings of cross-linking agents.

The results of T_g measurements of fully cured samples are shown in Fig. 5. These T_g values were determined from the inflection point of the stepwise transition during dynamic temperature scans at 10°C min^{-1}. As expected, the glass transition temperature of the resulting networks increases with increasing loadings of cross-linking agents for CL-2 and CL-3. Since the molecular masses of the cross-linking agents vary significantly, the cross-

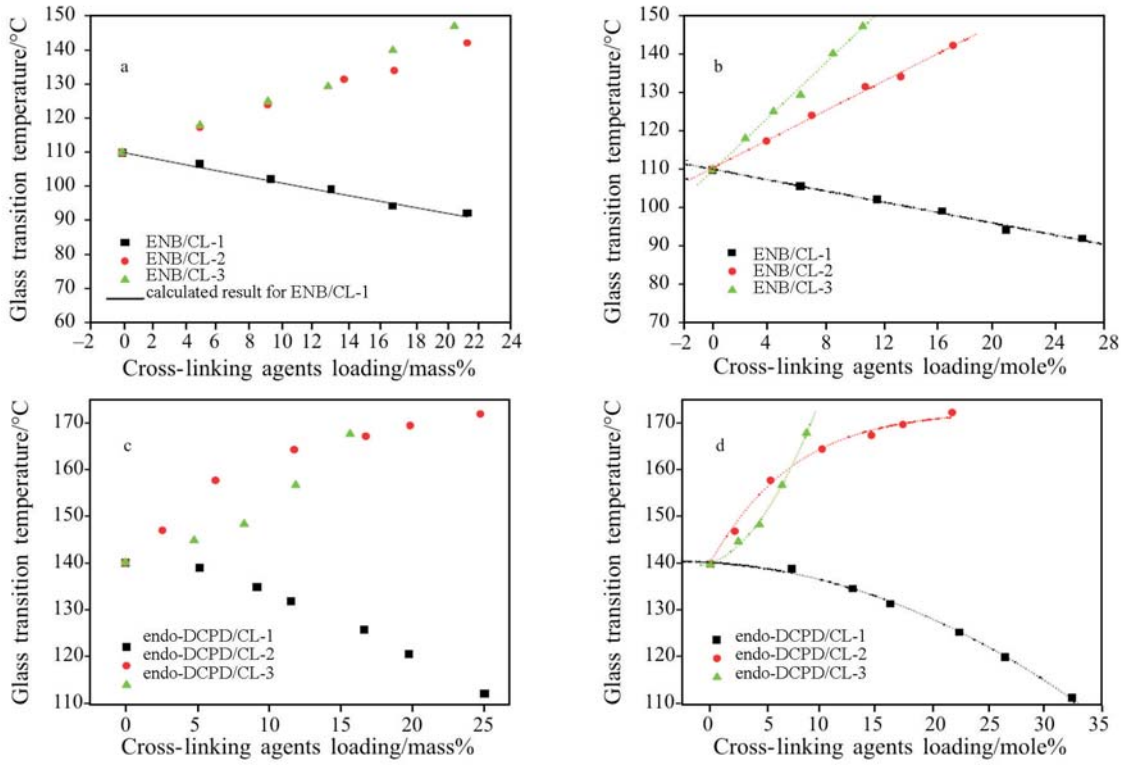

Fig. 5 Effect of cross-linking agents on the glass transition temperature of the thermosets

linking agent loadings are plotted on both a mass% and mole% basis in Fig. 5.

While the addition of CL-2 and CL-3 results in a monotonic increase in the glass transition temperature for both ENB (Figs 5a and b) and *endo*-DCPD (Figs 5c and d); the addition of CL-1 causes a reduction in T_g with increasing loading levels for both systems. Obviously, CL-1 is not an effective cross-linking agent. After incorporation of CL-1 into the polymer structure, the remaining ring becomes a disubstituted cyclopentadiene, similar to the cyclopentene group in poly-DCPD, and is less reactive [14]. The DSC scan curves for each ENB/CL-1 sample showed only one T_g. Therefore, ENB/CL-1 systems are polymerized to form random copolymers. The T_g of the ENB/CL-1 system can be calculated by the Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where T_{g1} and T_{g2} represent the glass transition of the component polymers and w_1 and w_2 are the mass fractions.

The T_g of poly-ENB was measured as 110°C and T_g of poly-norbornadiene (CL-1) was reported as 35°C [15]. The calculated results match very closely with the experimentally measured glass transitions and are shown for each mass fraction in Table 1. The residue cyclopentene groups of the polymerized CL-1 are more stable to olefin metathesis than the norbornene ring and fail to form a cross-linking network with poly-ENB. Similar results are observed in *endo*-DCPD/CL-1 systems: with the increasing loadings of CL-1, the glass transition temperatures of the systems decrease. The only difference is that T_g does not have a linear relationship with CL-1 loading because *endo*-DCPD can homogeneously polymerize as a cross-linked network without any cross-linking agents. As with the ENB/CL-1 system, the reduction in T_g indicates that CL-1 does not increase the degree of cross-linking in the *endo*-DCPD/CL-1 blends.

In great contrast, as the CL-2 and CL-3 loadings increase, the T_g of the ENB and *endo*-DCPD systems also increase. This increase of T_g is a clear indication of the increasing degree of cross-linking in these systems. Both CL-2 and CL-3 have two norbornene rings, each with equal metathesis reactivity that is similar to the reactivity of the norbornene ring of ENB. Once one of the two norbornene rings of CL-2 and CL-3 polymerize, the other norbornene rings will undergo further reactions without a decrease in reactivity. From the chemical structure, the two norbornene rings of CL-3 are separated by a benzene ring and are independent of each other. Therefore, the remaining norbornene ring is less affected by the other ring being incorporated into the growing polymer network and has more space to move, and a greater chance of reacting with other norbornene rings of monomer, cross-linking agents, and polymer chains. Compared with CL-2, similar loading of CL-3 increase the T_g more, as shown in Fig. 5b (the mass fraction loading of cross-linking agents were converted to mole fraction based on the molecule mass of the monomer and cross-linking agents). For example, with 10.8% (mole fraction) loading of CL-2, the T_g for an ENB/CL-2 mixture is 131°C; with almost the same loading of CL-3 (10.6%), the T_g for an ENB/CL-3 mixture is increased to 147°C.

Table 1 Calculated T_g of ENB/Cl-1 system

Mass%	Mol%	Meas. T_g/°C	Calc. T_g/°C
0	0	110	110
4.8	6.2	106	106
9.2	11.6	102	102
12.9	16.2	99	98
16.7	20.7	94	95
21.3	26.1	92	91

Because *endo*-DCPD can form a cross-linked network without addition of cross-linking agents, the influence of cross-linking agents is more complicated. For the *endo*-DCPD/CL-2 system, once ROMP polymerization is initiated by Grubbs' catalyst, a poly-DCPD network forms even at low degrees of cross-linking. The formed network limits the motion of cross-linking agents and un-reacted norbornene rings of the cross-linking agents and polymer chains. As shown in Fig. 5c, although T_g is increased with increasing CL-2 loading, the rate of increase with CL-2 loading decreases at higher mass fraction.

As mentioned before, the two norbornene rings of CL-3 are separated by a benzene ring and independent of each other. CL-3 shows very different effects on the glass transition of the *endo*-DCPD system. In this case, the rate of T_g increases with CL-3 loading. At higher CL-3 loadings there may be a plateau, with T_g only increasing slightly with higher cross-linker loadings. However, to date, there is no experimental data to prove this trend because of difficulties in sample preparation. It is hard to dissolve solid CL-3 (m.p. 71.0°C) in *endo*-DCPD.

Conclusions

The reactivities of monomers *endo*-DCPD, *exo*-DCPD and ENB were evaluated by exothermic peak locations at various heating rates by DSC measurements. The results showed that ENB has the highest ROMP reaction activity. Polymerization

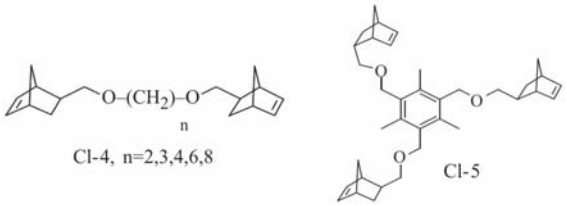

Fig. 6 Additional cross-linking agents to be investigated

kinetics of ENB mixtures with custom cross-linking agents (CL-2) were also evaluated by DSC. Cross-linking agents have no obvious effects on the polymerization kinetics of the ENB/CL-2 system, because both monomer and cross-linking agents have similar reaction groups.

The influence of cross-linking agents on the glass transition of *endo*-DCPD and ENB was investigated in details. With increasing loading of cross-linking agent CL-1, both *endo*-DCPD and ENB systems showed decreased glass transition temperatures. However, with the addition of CL-2 and CL-3, both *endo*-DCPD and ENB systems showed monotonic increases in T_g. Because of different chemical structures, CL-2 and CL-3 have different effects. On a mole fraction basis, CL-3 is more efficient at increasing the degree of cross-linking.

We are currently working on additional cross-linking agents (CL-4 and CL-5 in Fig. 6). CL-4 will allow investigation of homologous series of cross-linking agents to determine the influence of cross-linker length on T_g enhancement. CL-5 differs from previous cross-linking agents by being tri-functional rather than bi-functional and should result in even higher levels of cross-linking at lower loading levels. More experiments are also proceeding, such as swelling tests to determine the degree of cross-linking and dynamic mechanical analysis (DMA) for physical properties of monomer/cross-linking agent systems.

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