CURE CHARACTERIZATION AND VISCOSITY DEVELOPMENT OF RING-OPENING METATHESIS POLYMERIZED RESINS

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The ring-opening metathesis polymerization (ROMP) kinetics of three different norbornene-based monomers, ethylidene norbornene (ENB), *endo*-dicyclopentadiene (DCPD) and *exo*-DCPD, in the presence of Grubbs' catalyst are examined using differential scanning calorimetry and rheokinetic viscosity measurements. Several different parameters were considered, such as, the monomer healing agents (including different monomer mixtures), the catalyst concentration, and test temperature to determine how these parameters influence cure development. The polymerization kinetics, quantified by exothermic peak locations in the case of differential scanning calorimetry and rheokinetic transition times in the case of viscosity measurements, are shown to be highly dependent on monomer type and catalyst concentration. The ENB monomer had the fastest kinetics even at the lowest catalyst concentration compared to the other diene monomers and mixtures.

Introduction

With the development of highly tolerant ring-opening metathesis polymerization (ROMP) catalysts, such as ruthenium based Grubbs' catalyst [1], the synthesis of many polymers is being realized. One such polymer system is polydicyclopentadiene (poly-DCPD), a highly cross-linked polymer of high toughness. The cure kinetic behavior, and subsequent viscosity development, of these ROMP polymers is an important parameter in applications such as reaction injection molding (RIM) and resin transfer molding (RTM) [2]. These ROMP monomers and catalysts have also been encapsulated and incorporated into self-healing composite materials to autonomically repair microcracks when the composite is damaged [3, 4]. In these self-healing applications, the polymerization kinetics determine the extent to which polymerization can occur inside the microcracks for a given time and at a particular temperature and, therefore, the healing efficiency.

Another promising ROMP monomer for RTM and self-healing applications is 5-ethylidene-2-norbornene (ENB), which polymerizes into a linear polymer or can be blended with DCPD to form a cross-linked network [5]. The chemical structures for DCPD and ENB monomers are shown in Fig. 1 below.

The polymerization, initiated by the ruthenium/alkylidene complex (Grubbs' catalyst), of both DCPD and ENB is highly exothermic because of the relief of ring strain energy. Figure 2 illustrates the ROMP mechanism for the DCPD system. First the ruthenium metal carbene and the cycloalkene combine to form an intermediate metallacyclobutane. The metallacycle then breaks between the atoms that initially shared a double bond and the new olefin that is generated remains attached to the catalyst as part of a growing polymer chain (driven by the ring strain relief). The remaining double bond may be polymerized in a similar way to form a cross-linked poly-DCPD network.

DCPD can exist in two sterio-isomer forms, *endo*-DCPD and *exo*-DCPD [6], as seen in Fig. 3. Recent studies using in situ NMR have shown that *exo*-DCPD is more reactive than *endo*-DCPD for ROMP primarily for steric reasons [7]. Since commercial suppliers do not produce pure *exo*-DCPD it is necessary to synthesize it from the commercially available *endo*-isomer.

In this paper we report on the use of differential scanning calorimetry (DSC) and rheokinetics to evaluate the polymerization of *endo*-DCPD, *exo*-DCPD, ENB, and their mixtures. Rheokinetics, the study of the polymerization by means of rheological measurements performed during the polymerization, coupled with DSC, allows us to correlate viscosity development with degree of cure.
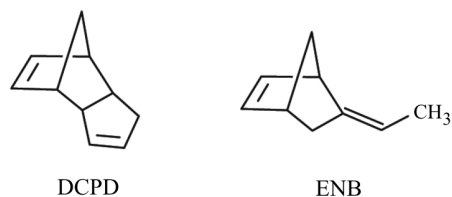

Fig. 1 DCPD and ENB structures

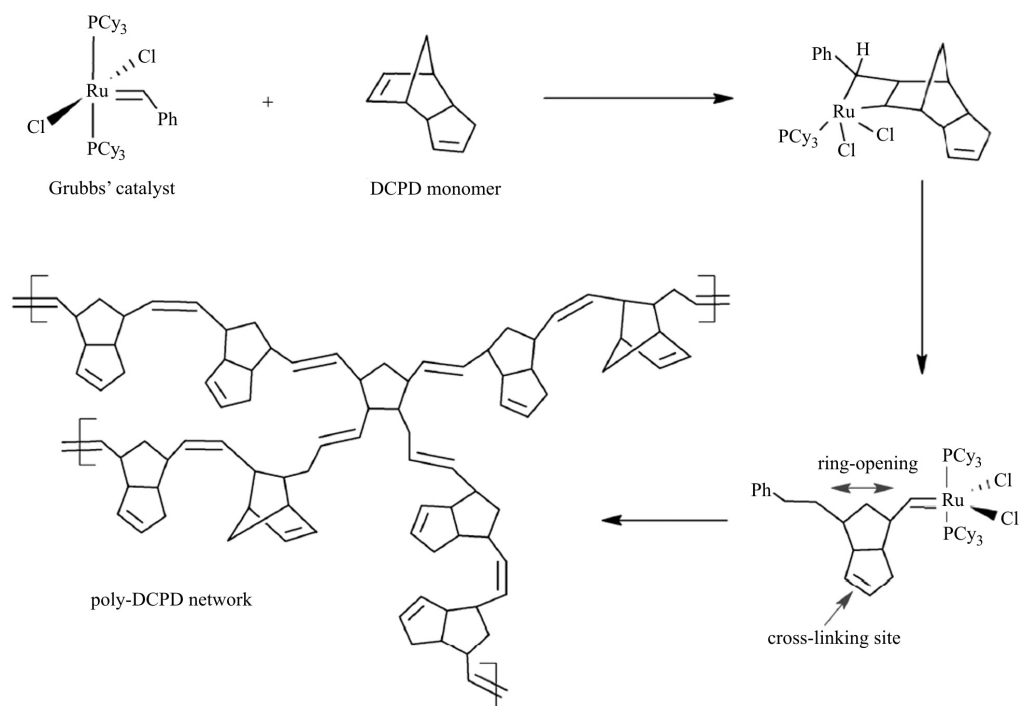
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Fig. 2 Ruthenium-based Grubbs' catalyst initiating the ROMP of DCPD. The result is poly-DCPD, a tough, rigid thermoset of excellent impact strength
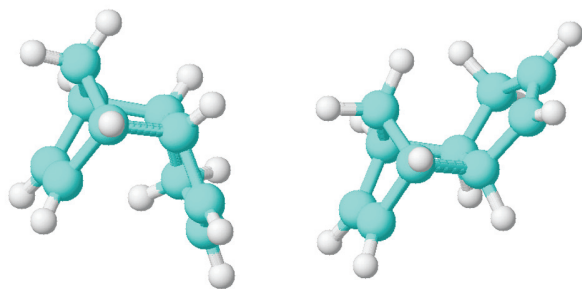

Fig. 3 Left – *endo*-DCPD and right – *exo*-DCPD

Experimental

DCPD and ENB monomers were purchased from Fisher Acros Organics (Somerville, NJ, USA) and Sigma-Aldrich Inc. (Milwaukee, WI, USA), respectively. As supplied, the DCPD monomer was predominatly *endo*-isomer. Bis(tricyclo-hexylphosphine) benzilidene ruthenium(IV) dichloride (Grubbs' catalyst) was also purchased from Sigma-Aldrich. *Exo*-DCPD was synthesized from the *endo*-isomer by a slight modification of literature methods [8, 9]. Four different monomer mixtures were analyzed throughout this investigation: ENB, *endo*-DCPD, *exo*-DCPD, and a 1:1 volume ratio of ENB and *endo*-DCPD. The mixing of the monomers with Grubbs' catalyst initiates the ROMP reaction (e.g. Fig. 2). This ROMP reaction can be extremely rapid at room temperature, the rate depending on the catalyst concentration, the monomer used, and sample size.

DSC technique

The polymerization of ENB, *endo*-DCPD and *exo*-DCPD was accomplished with three different catalyst/monomer ratios, as shown in Table 1. Since the polymerization rate is fastest for ENB, the amount of required catalyst is significantly lower for ENB than for the DCPD isomers. Between 2 and 10 mL of monomer were added to vials containing 0.6 to 10 mg of catalyst (depending on the concentration required) and the vials were vigorously mixed for less than 15 s to dissolve the catalyst powder, forming a homogeneous solution. The vials were then pored streamwise over a fine steel mesh and into a vat of liquid nitrogen to create small frozen droplets of catalyzed

Table 1 Catalyst concentrations analyzed by DSC

Designation	*Endo*-DCPD catalyst (g)/DCPD (mL)	*Exo*-DCPD catalyst (g)/DCPD (mL)	ENB catalyst (g)/ENB (mL)
low	$1.33 \cdot 10^{-3}$	$1.33 \cdot 10^{-3}$	$0.20 \cdot 10^{-3}$
medium	$2.00 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$0.50 \cdot 10^{-3}$
high	$2.67 \cdot 10^{-3}$	$2.67 \cdot 10^{-3}$	$0.80 \cdot 10^{-3}$

monomer (diameter ca. 1 mm). Small frozen beads of catalyzed monomer were placed into aluminum DSC pans and loaded into the DSC chamber at a standby temperature of –50°C.

DSC measurements were performed with a Mettler Toledo DSC821^e. The DSC cell was swept by a constant flow of nitrogen at 80 mL min^{-1}. Dynamic heating tests were performed on the monomer/catalyst systems at various heating rates over a temperature range of –50 to 200°C.

Rheokinetics technique

The change in viscosity with respect to time was studied considering the following variables: monomer system used, catalyst concentration, and test temperature. A cone and plate viscometer (Brookfield CAP 2000+) was used to measure the viscosity development with time for the four monomer systems mentioned above in the presence of Grubbs' catalyst at constant temperature. For the *endo*-DCPD tests, the concentration was varied from 3.0 to 30 mg mL^{-1}; for ENB, the concentration was varied from 0.05 to 0.5 mg mL^{-1}; for the ENB/DCPD mixture, the concentration was varied from 1.67 to 4.0 mg mL^{-1}; finally, for the *exo*-DCPD tests, the concentration was varied from 0.125 to 1.0 mg mL^{-1}. After the catalyst was weighed in a vial, the appropriate amount of monomer was added to the vial and quickly mixed. The time was measured starting from the instant the monomer and catalyst were combined. After a brief period of agitation, a thin film was poured onto the viscometer's plate. The cone was then lowered onto the film to start recording viscosity measurements at isothermal temperatures ranging from 5 to 40°C.

Results and discussion

DSC

Five typical DSC scans for *endo*-DCPD at a high concentration (2.67 mg mL^{-1}) are shown in Fig. 4. The end of a broad endothermic region that extends from –5 to 15°C is present which corresponds to the melting of DCPD. As expected, as the heating rate increases the peak temperature also increases. For the other catalyst concentrations (medium and low) the results are qualitatively similar except that as the catalyst concentration decreases, the exothermic peak shifts to higher temperatures for a given heating rate.

In our previous kinetic modeling work of the cure kinetics of *endo*-DCPD [10], the endothermic melting peak was disregarded by constructing a best fit spline connecting the premelt and postmelt regions to effectively eliminate the melting phenomenon from

the heat flow curves to simplify the kinetic analysis (arguing that less than 0.5% of cure advancement occurs before the end of the melting region). In that work [10], the experimental data were used to test several different phenomenological kinetic models, where the degree of cure is identified as an internal state variable, $\alpha(t)$, defined as the ratio of the enthalpy of reaction up to time t, $H(t)$, to the total enthalpy of reaction, H_R. The data were best modeled with a model-free isoconversional method and revealed that the activation energy increased significantly for degrees of cure greater than 60%.

The corresponding DSC results for the *exo*-DCPD at the same high concentration level (2.67 mg mL^{-1}) are shown in Fig. 5 and have two primary differences than the *endo*-isomer experiments. First, the reaction has two distinct exothermic peaks at high heating rates. The second peak is not distinguishable at 2.0 K min^{-1} but begins to emerge at 5.0 K min^{-1} and becomes even more separable from the first exothermic peak as the heating rate increases. The second difference between the *endo*- and *exo*-DCPD DSC curves is the location and form of the
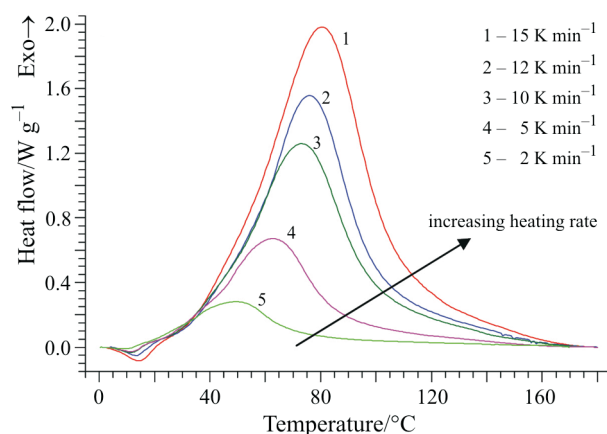
Fig. 4 *Endo*-DCPD at high concentration (2.67 mg mL^{-1}) showing one peak
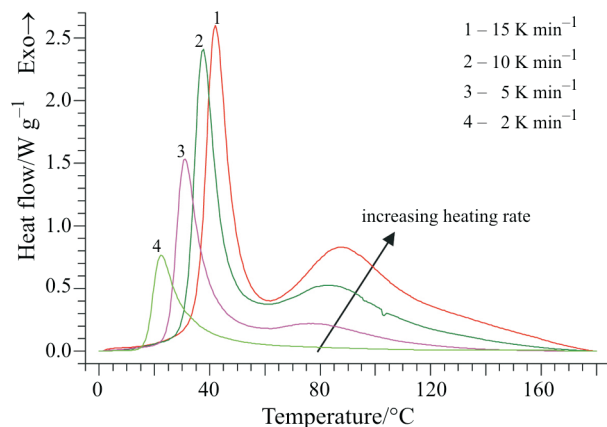
Fig. 5 *Exo*-DCPD at high concentration (2.67 mg mL^{-1}) showing two peaks

primary (first) exothermic peak. With the exo-DCPD the first peak occurs at much lower temperatures compared to endo-DCPD experiments at the same heating rates and catalyst loading levels.

The presence of two peaks is an indication that there are at least two steps in the reaction, and it is theorized that the first peak corresponds to the ring-opening of the initial norbornene ring, while the second peak corresponds to the ring-opening of the additional cross-linking sight (Fig. 2). It should be expected based on the work by Rule and Moore [7], that the kinetics of the ROMP of the first norbornene ring is faster in the *exo*-DCPD than the *endo*-DCPD for steric reasons. However, the kinetics of the ROMP of the additional cross-linking site should not change significantly from *endo*- to *exo*-DCPD. In the case of the *endo*-DCPD, the kinetics of the ring-opening for both peaks is similar, so the multiple peaks are constructively combined into one broader peak. However, even in the kinetic analysis we reported earlier on the cure characterization of the ROMP of *endo*-DCPD [10], it was reported that the activation energy determined by a Friedman analysis [11] as a function of conversion level (degree of cure) was not constant, an indication that the best reaction model involves at least two steps, even for the *endo*-DCPD with only one apparent exothermic peak.

From experience, the ENB was known to polymerize the fastest of all three diene monomers even at much lower catalyst loadings. A typical set of DSC curves for ENB with just 0.8 mg mL^{-1} of catalyst to monomer is shown in Fig. 6. Like both the *endo*-DCPD and *exo*-DCPD, the experiments run at all three catalyst loadings (low, medium, and high per Table 1) were qualitatively similar, but shifted to lower temperatures (faster kinetics) with increased catalyst loading. In contrast to the *exo*-DCPD, the ENB monomer showed only one exothermic peak 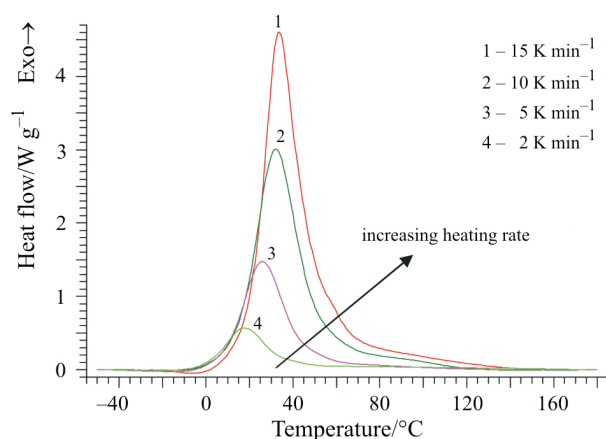in each dynamic DSC experiment. This is expected since the polymerized ENB is a linear polymer without the extra cross-linking site to undergo network formation via an additional kinetic step.

Rheokinetics

As an alternative complimenting technique to characterize the cure behavior of the diene monomers in the presence of Grubbs' catalyst, rheokinetic measurements can characterize mechanical flow properties (viscosity) throughout the curing process. The dramatic increase in viscosity is an important parameter to understand when designing manufacturing process conditions. A typical curve from rheokinetics cone and plate viscosity experiments is shown in Fig. 7 below.

As with other rheokinetics data for polymers [12–14], the experimental rheometric data could generally be well fitted by two power laws with one power law fitting the data before a transition time and the other power law fitting the data after the transition time. The transition time, t_t, (border between the two power law trends) is calculated to maximize the correlation coefficients (R^2) of the least squares best fit to the data. Initially, we planned to use this transition time, as well as the difference between the two power law exponents, b_1 and b_2, to quantify and compare the reaction kinetics for the diene monomers and conditions. However, upon detailed data analysis it was found that the transition time always occurred approximately when the viscosity reached 1 Pa s. Also, because of uncertainty and scatter in the low viscosity measurements in region I, the quantity Δt, defined as the time for the viscosity to go from 1 to 15 Pa s, was

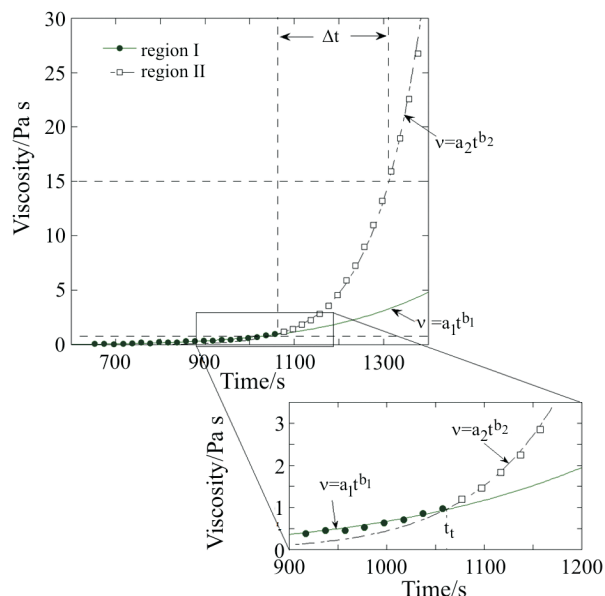**Fig. 6** ENB at med. concentration (0.8 mg mL^{-1}) showing one peak

Fig. 7 Typical rheokinetics curve of diene monomer in the presence of Grubbs' catalyst

determined to be a better measure to quantify the reaction rate. These two values, t_t and Δt, quantify how long it takes for the polymerization to initiate and how quickly the reaction progresses after initiation respectively. Presumably, the polymerization initiation (t_t) is at least partially related to phosphine-ligand dissociation in the monomer while Δt relates primarily to the catalyst/monomer reactivity [15].

Multiple experiments on *endo*-DCPD, *exo*-DCPD, ENB, and a 1:1 volume ratio of *endo*-DCPD and ENB (labeled as '*endo*-DCPD/ENB mixture' in subsequent figures) with catalyst concentrations ranging from 0.03 to 30 mg mL^{-1} were conducted and are summarized in terms of Δt and t_t parameters in Fig. 8 at 25°C. Each monomer could only be experimentally tested successfully over a certain range of concentrations because of kinetic limitations. For example, at room temperature, *endo*-DCPD would not polymerize at very low concentrations (below 1 mg mL^{-1}) within a reasonable timeframe, while ENB would polymerize too fast at very high concentration (above 1 mg mL^{-1}), before meaningful measurements could be taken using the viscometer.
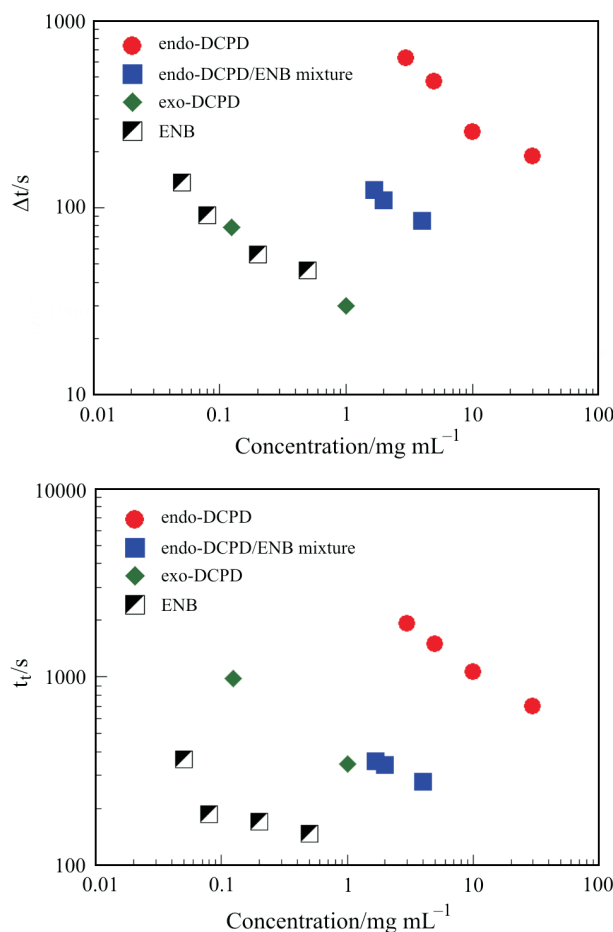

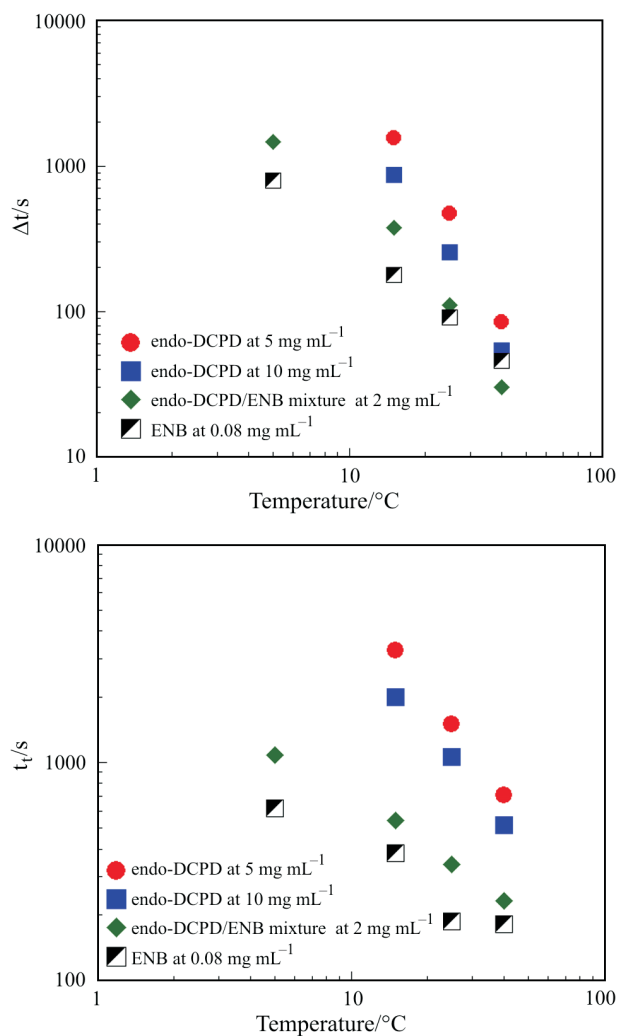**Fig. 8** Effect of catalyst concentration on the reaction parameters, Δt and t_t at 25°C

Fig. 9 Effect of temperature on the reaction parameters, Δt and t_t at various catalyst concentrations

Figure 8 illustrates that for all of the monomer systems, when the catalyst concentration increases, Δt and t_t, decrease. Both ENB and *exo*-DCPD have similar Δt behavior *vs.* concentration, but the initiation for the ROMP, quantified by t_t, is significantly faster for the ENB.

As expected, as the isothermal testing temperature increased so did the polymerization rate, indicated by a decrease in both Δt and t_t, as illustrated in Fig. 9. The pure *endo*-DCPD could not be tested at the lowest temperature, 5°C, because the polymerization rate was too slow even at relatively high catalyst loadings. The mixture of *endo*-DCPD with ENB has been shown in other work [16] to be miscible in all proportions and to create a cross-linked copolymer of polyDCPD/ENB. From this work, the mixture of *endo*-DCPD with ENB is shown to have polymerization kinetics between the neat *endo*-DCPD and neat ENB.

Conclusions

The polymerization kinetics, quantified by exothermic peak locations for a given dynamic heating rate in the case of DSC measurements and by kinetic parameters Δt and t_t in the case of rheokinetics measurements, are shown to be highly dependent on monomer type and catalyst concentration. The ENB monomer had the fastest kinetics even at the lowest catalyst concentrations compared to the other diene monomers and mixtures. Also, the *exo*-DCPD monomer polymerized significantly faster than the *endo*-isomer of DCPD, confirming previously published NMR results [7]. The presence of two exothermic peaks at high heating rates in the dynamic DSC experiments of *exo*-DCPD indicate the presence of a complex, multi-step reaction process that could be related to the difference in the ROMP kinetics between the two strained cyclic rings in the DCPD monomer. Additional analysis to develop multi-step cure kinetic models which fit this data is ongoing. With these models the relationship between degree of cure determined from DSC experiments can be coupled with the rheokinetic data to correlate viscosity development with degree of cure.

Acknowledgements

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