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14. ABSTRACT The co-cyclotrimerization of two tricyanate ester monomers, Primaset PT-30 and 1,2,3-tris(4-cyanato)propane (FlexCy) in equal parts by weight with Primaset LECy, a liquid dicyanate ester, was investigated for the purpose of exploring synergistic performance benefits. The monomer mixtures formed stable, homogeneous blends that remained in the supercooled liquid state for long periods at room temperature, thereby providing many of the processing advantages of LECy in combination with significantly higher glass transition temperatures (315–360 °C at full cure) due to the presence of the tricyanate-derived segments in the conetwork. Interestingly, the glass transition temperatures of the conetworks after cure at 210 °C, at full cure, and after immersion in 85 °C water for 96 h were all higher than predicted by the Flory–Fox equation, most significantly for the samples immersed in hot water. Conetworks comprising equal parts by weight of PT-30 and LECy retained a “wet” glass transition temperature near 270 °C. The onset of thermochemical degradation for conetworks was dominated by that of the thermally less stable component, while char yields after the initial degradation step were close to values predicted by a linear rule of mixtures. Values for moisture uptake and density in the conetworks also showed behavior that was not clearly different from a linear rule of mixtures. An analysis of the flexural properties of catalyzed versions of these conetworks revealed that, when cured under the same conditions, conetworks containing 50 wt % PT-30 and 50 wt % LECy exhibited higher modulus than networks containing only LECy while conetworks containing 50 wt % FlexCy and 50 wt % LECy exhibited a lower modulus but significantly higher flexural strength and strain to failure. Thus, in the case of “FlexCy”, LECy was copolymerized with a tricyanate that provided both improved toughness and a higher glass transition temperature					
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Supporting Information

“Synergistic Physical Properties of Co-Cured Networks Formed from Di- and Tri-cyanate Esters”

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S1. Additional Image from X-Ray Crystallographic Data for Primaset® LECy

The crystals obtained for LECy showed a significant amount of disorder despite the collection of data at low temperatures. In this case it is believed the disorder is due to the presence of primarily two distinct crystal forms. Figure S1-1 shows these two forms overlaid (with 50% thermal ellipsoids).

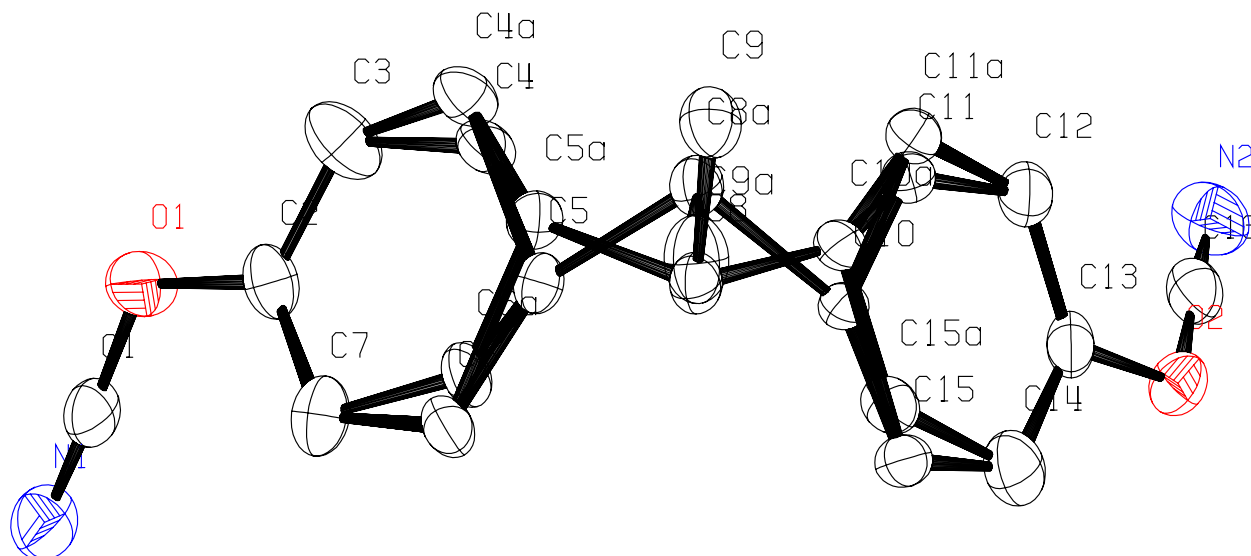


Figure S1-1. Overlay of two primary crystal forms for Primaset® LECy.

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S2. Glass Transition Temperatures at Full Cure for Polycyanurate Networks with LECy, PT-30, and FlexCy.

Although they are thermochemically quite stable compared to many other thermosetting networks, polycyanurate networks do undergo some thermochemical degradation at temperatures well below the 5% onset of decomposition point (typically 400-450 °C). The degradation produces enough heat at temperatures above about 350 °C to interfere with Differential Scanning Calorimetry (DSC) scans, meaning glass transition temperatures and other significant features are usually not detectable via standard (non-modulated) DSC. Of the five polycyanurate networks studied (Primaset® LECy, Primaset® PT-30, FlexCy, and the 50/50 wt% co-networks of PT-30 / LECy and FlexCy / LECy, only two (LECy and FlexCy / LECy) had glass transition temperatures at full cure that were detectable by standard DSC.

Standard DSC scans for mixtures of LECy with FlexCy and with PT-30, after heating to 350 °C to achieve full cure, are shown in Figures S2-1 and S2-2. Features identified as T_G 's have been circled. Some traces also appear to show a slight feature near 270 °C that, given its appearance at the same temperature repeatedly, may be an artifact. As expected, there is a uniform progression towards a higher T_G as the amounts of FlexCy and PT-30 increase, but for PT-30, a T_G is visible only at 20 wt%. Since the visible T_G values are all below 350 °C, networks that show a T_G have also been heated past their individual T_G 's, ensuring that the maximum possible extent of cure was achieved. Previous DSC/FT-IR studies have also shown that LECy achieved complete conversion of cyanate ester groups when heated to 350 °C in the DSC. We are therefore highly confident in the reported T_G values for the LECy (which has been measured previously by us at 295 °C)^{S1} as well as the FlexCy / LECy samples.

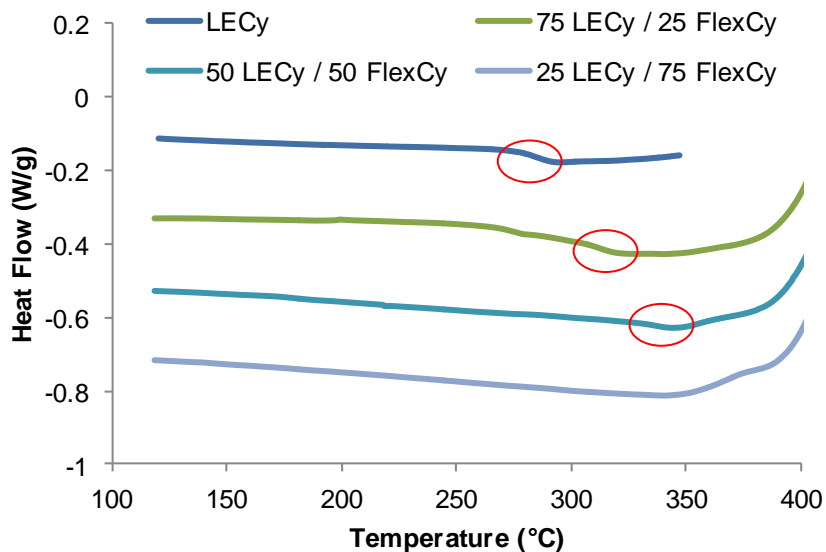


Figure S2-1. Standard DSC of LECy and co-networks with FlexCy, heated at 10 °C/min. after previous heating to 350 °C (also at 10 °C/min.). Curves have been offset for clarity.

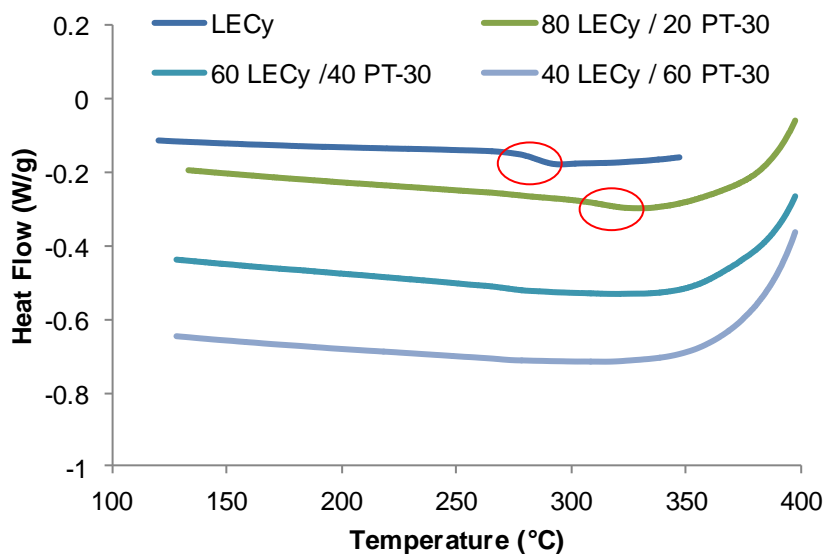


Figure S2-2. Standard DSC of LECy and co-networks with PT-30, heated at 10 °C/min. after previous heating to 350 °C (also at 10 °C/min.). Curves have been offset for clarity.

For the other three networks, standard DSC scans produced no detectable T_G up to 350 °C. In this situation, there are two major issues that must be resolved. The first is reliably detecting a T_G in the midst of heat flow signals from cure and/or decomposition. Modulated DSC can detect a T_G via step change in heat capacity when cure and/or degradation are present, however, modulation of the DSC signal requires a slow heating rate, which in turn necessitates long exposure times at elevated temperatures for the samples. As long as the rate of network degradation is slow enough, the separation of reversible (heat capacity) and non-reversible (degradation and cure) signals can be achieved for a reasonably in-tact network. Mechanical methods, such as oscillatory thermomechanical analysis (TMA) can also be helpful because they can often detect the onset of loss in stiffness or increase in thermal expansion that takes place slightly below the glass transition temperature. Like DSC, however, samples degrade above 350 °C, which limits the maximum temperature that can be utilized.

Figures S2-3 through S2-7 show modulated DSC scans (modulation amplitude 1 °C, modulation period 40 s, average heating rate 5 °C/min.) for samples previously heated to 350 °C (via a fast ramp in the DSC) of LECy, FlexCy / LECy (50 wt% each), FlexCy, PT-30 / LECy (50 wt% each), and PT-30, respectively. The average heating rate was kept high in order to prevent degradation of the networks. The reversible heat flow signals are somewhat noisy, but for LECy, the LECy / FlexCy blend, and FlexCy, a step change indicating a T_G is clearly seen. For both LECy and the LECy / FlexCy blend, the T_G from modulated DSC (296 °C and 340 °C, respectively), matches that seen in standard DSC, while for FlexCy the T_G is 370 °C. For PT-30, there is a possible T_G near 350 °C, while for the PT-30 / LECy network, no step change is clearly visible, though a feature consistent with a T_G onset is seen at around 365 °C. Modulated DSC

thus appears to have been somewhat successful in identifying a glass transition temperature for these networks.

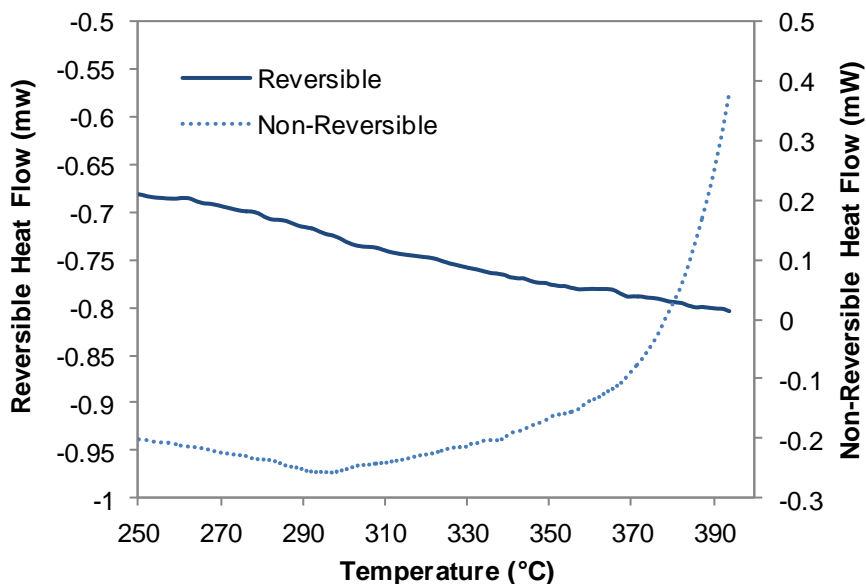


Figure S2-3. Modulated DSC of LECy after heating to 350 °C.

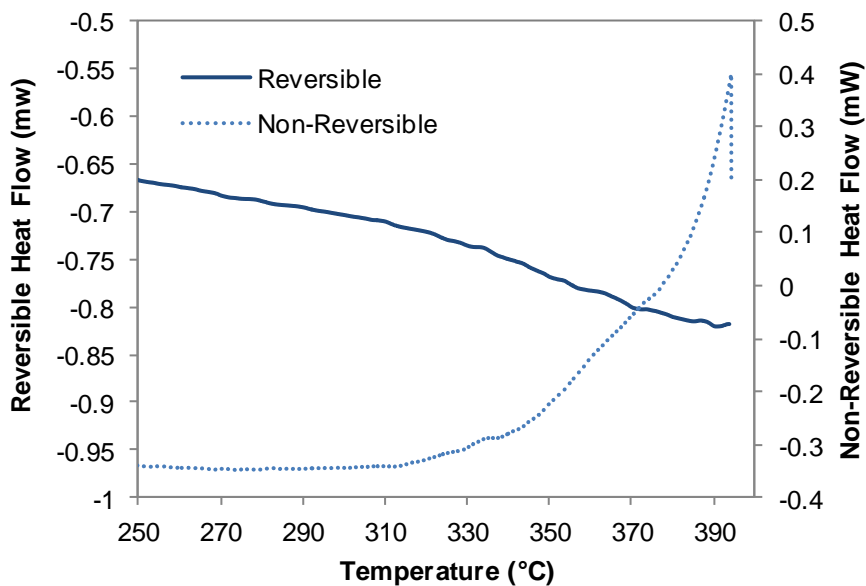


Figure S2-4. Modulated DSC of 50 wt% FlexCy / 50 wt% LECy after heating to 350 °C.

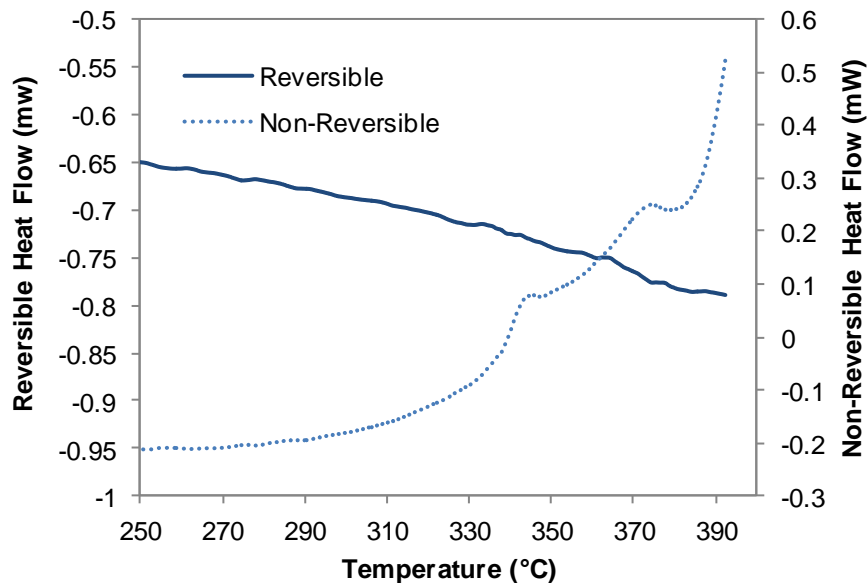


Figure S2-5. Modulated DSC of FlexCy after heating to 350 °C.

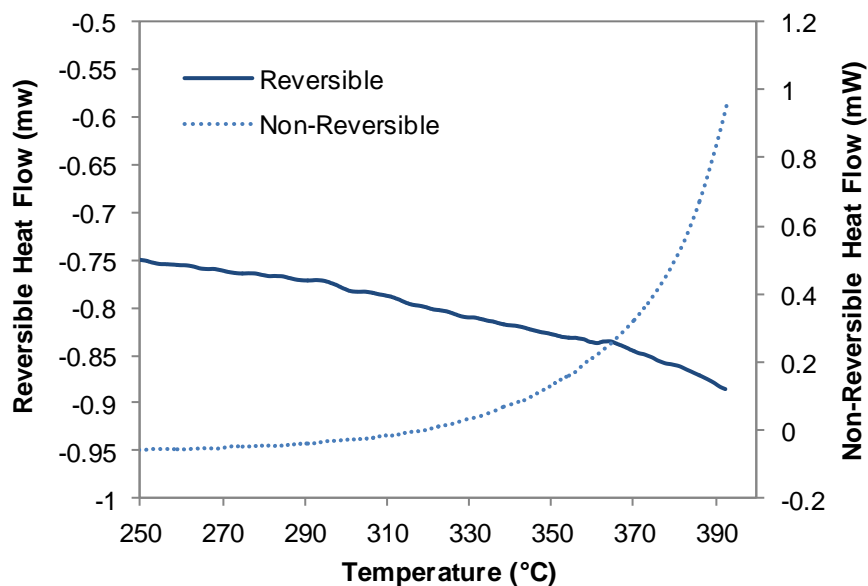


Figure S2-6. Modulated DSC of 50 wt% PT-30 / 50 wt% LECy after heating to 350 °C.

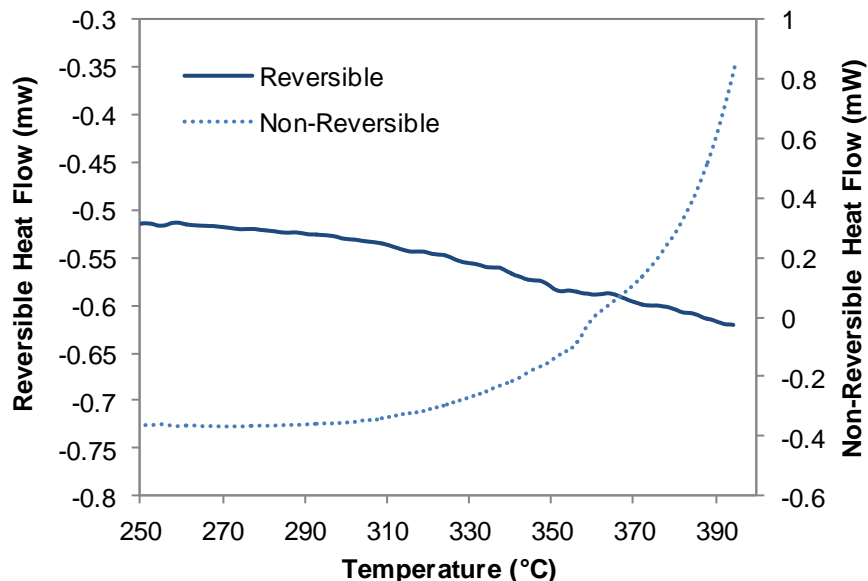


Figure S2-7. Modulated DSC of PT-30 after heating to 350 °C.

In addition to the fact that some of the T_G signals in the modulated DSC scans are weak compared to the noise, a more important issue is lack of information about the extent of cure that corresponds to the T_G (the is the second of the two issues mentioned earlier for DSC scans of polycyanurate networks with a T_G above 350 °C). For samples with a T_G below 350 °C, the previous heating to 350 °C will have enabled complete cure to take place. For samples with a T_G of 350 °C or higher, the previous heating will have caused vitrification (due to cure) but, afterward, the samples will have remained vitrified up to the point at which a T_G is detected. In the vitrified state, the attainment of full conversion is not guaranteed. Therefore, in addition to modulated DSC, an investigation of the extent of cure for samples heated to 350 °C is also required.

FT-IR spectroscopy provides a simple and convenient way to assess whether or not full conversion has been achieved in polycyanurate networks. Previous studies by FT-IR have shown that comparatively, much higher conversions are achieved in FlexCy than in PT-30 when

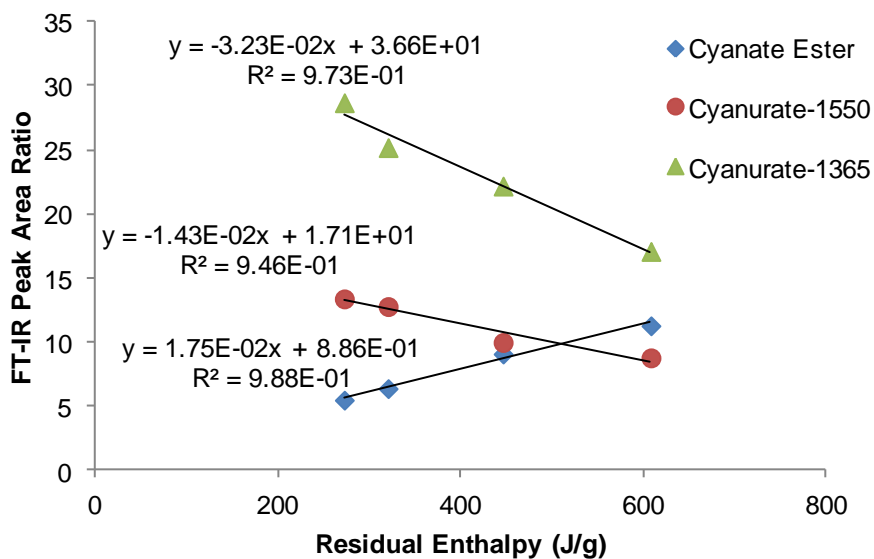


Figure S2-8. DSC/FT-IR plot for catalyzed PT-30 cured at 150 °C for 30, 60, 120, and 240 minutes.

cured at very high temperatures.^{S2} The extent of conversion in PT-30 when heated to 350 °C was determined by a combined DSC / FT-IR technique that relies on the linearity of signal to conversion measurements in both techniques.^{S3} Figure 2-8 shows the FT-IR intensities for three absorbance peak area ratios, the cyanate ester peak near 2250 cm⁻¹, the cyanurate peak near 1365 cm⁻¹, and a second cyanurate peak near 1550 cm⁻¹, normalized to the area of the phenyl peak near 1500 cm⁻¹, as a function of the residual enthalpy of cure measured upon heating samples to 350 °C in the DSC. As demonstrated previously, when different cure conditions (in this case, 150 °C for 30, 60, 120, and 240 minutes for catalyzed PT-30 samples) were examined, linear relationships were found between the residual enthalpy of reaction and the absorbance intensity ratios. For the cyanate ester peak, the x-intercept of a linear regression line through the points provides an estimate of the enthalpy of cure that is needed to achieve complete cure even after heating to 350 °C. As shown previously, for cyanate esters with T_G values at full cure below 350

°C, this estimate will not be significantly different from zero. For PT-30, the value is 50 ± 40 J/g, which, compared to the measured enthalpy of cure of 740 ± 60 J/g for samples heated to 350 °C, yields a total enthalpy of cure of 790 ± 70 J/g (100 kJ/eq.) for PT-30 and a conversion of $94 \pm 6\%$ for cure to 350 °C. Since FlexCy is known to exhibit a higher conversion than PT-30 under similar cure conditions,^{S2} it is unlikely that the FT-IR technique would yield a conversion significantly different than 100% for samples of FlexCy heated to 350 °C.

Thus, although the DSC/FT-IR method provides some important information, more sources of information are needed to reach a more definitive conclusion. For PT-30, dynamic mechanical thermal analysis (DMTA) has shown a T_G at full cure near 400 °C.^{S4} Although some degradation of the network may interfere with the DMTA signal at this temperature, such degradation would likely result in a T_G measurement that is too low rather than too high. Oscillatory TMA data previously reported by us also showed a lower limit of 389 °C for the T_G of PT-30 at full cure. Given consistent values of 0.35-0.4 for the parameter λ in the diBenedetto equation^{S6} for polycyanurates other than PT-30 (see Section S4, as well as Table 1 in the main manuscript), a similar value for λ for PT-30 is a reasonable assumption. A T_G at full cure near 400 °C would produce the observed T_G of 350 °C at a conversion of 95-96% with $\lambda = 0.35-0.4$, in accordance with the results from DSC/FT-IR. Since the goal of the efforts described in this section is to determine a T_G at full cure for PT-30, the literature value of 400 °C seems most appropriate, with the observed T_G from modulated DSC being explained by vitrification of the sample, which prevents the T_G from rising above 350 °C prior to measurement due to suppression of cure beyond about 95% conversion. Thus, the uncertainty in the DSC/FT-IR estimate of conversion is significantly larger than what we believe on the basis of the literature and diBenedetto data. An uncertainty for the T_G at full cure of ± 10 °C based on the variations

shown in Reference S4, and an uncertainty of $\pm 2\%$ for the conversion on heating to 350 °C based on the predictions of the diBenedetto equation, seems most appropriate.

For FlexCy, we have previously reported T_G values as high as 351 °C from oscillatory TMA measurements,^{S5} and on early batches precipitated in ethanol (as opposed to “standard” batches precipitated in isopropanol), a T_G value of 377 °C has been measured. We also have obtained an FT-IR estimate of 94% conversion^{S5} (based only on the relative change in the cyanate ester peak compared to uncured monomer, a technique that has quantitative limitations), for a sample of “standard” FlexCy cured at 290 °C for 30 minutes in the DSC as part of a reaction kinetics study.^{S2} The residual heating portion of the DSC curve for this sample shows an onset of residual cure at a temperature of around 305 °C. As explained in Section S3, this onset temperature is believed to provide the best available estimate of the T_G immediately after cure, due to *in-situ* heating during subsequent measurements, even when a ramp rate of 50 °C is used. Oscillatory TMA, for instance, showed a lower limit of 349 °C for the T_G of samples cured under these conditions, presumably due to *in-situ* cure. A reasonable value of 0.35-0.4 for λ in the diBenedetto equation and a T_G of 305 °C at 94% conversion is consistent with the diBenedetto equation when the T_G at full cure is 355 – 365 °C. Although this value can only be considered a rough estimate due to the many caveats outlined above, it does suggest that the T_G of FlexCy at full cure is unlikely to be much higher than 370 °C. Since FlexCy contains more flexible network segments than PT-30, a somewhat lower T_G at full cure compared to PT-30 also makes sense from a molecular point of view. Taken together, all the evidence therefore suggests that 370 °C is the best available estimate for the T_G at full cure and that full cure is achieved by heating the sample to 350 °C.

Finally, the T_G at full cure for the 50 wt% PT-30 / 50 wt% LECy network is not readily apparent from modulated DSC, and the extent of cure on heating to 350 °C is also not apparent. An oscillatory TMA scan (Figure S2-9) conducted at 10 °C / min. showed a T_G (loss modulus peak) at 313 °C during the first heating. At this slower heating rate, there is significant *in-situ* cure during the first heating, so the observed T_G is much higher than the actual “as cured” value. After heating to 350 °C, on the subsequent cooling, the scan showed a 43 °C upward shift of the temperature associated with the onset of a decline in the storage component of stiffness (an indicator of the onset of T_G). The onset of a step change in the coefficient of thermal expansion (not shown) for this sample was also shifted upward by 40 °C. Such a shift suggests a T_G based on the loss modulus peak (which has been shown to coincide with DSC measurements)^{S7} of 353 - 356 °C. Such a value makes sense given vitrification of the sample would prevent a T_G value much higher than this on heating to 350 °C with no dwell time, however it only sets a lower limit on the T_G at full cure since the conversion of samples heated to 350 °C is unknown, and, like PT-30, could be less than 100%.

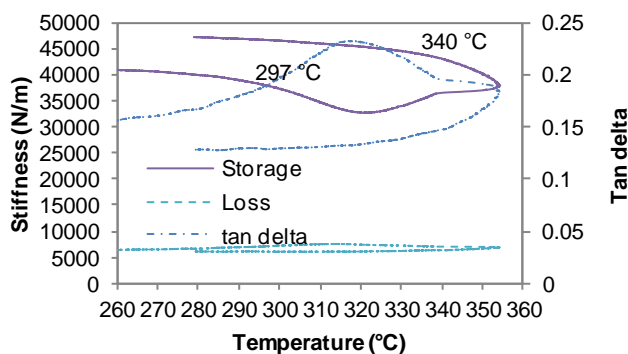


Figure S2-9. Oscillatory TMA scan of 50 wt% PT-30 / 50 wt% LECy cured at 210 °C for 24 hours, then heated at 10 °C/min in the TMA. Note that a substantial amount of *in-situ* cure takes place, so the “as cured” T_G is much lower (about 270 °C by DSC).

Although FT-IR spectroscopy is possible on samples heated to 350 °C, the absence of a cyanate ester peak could be attributed to either cure or to side reactions, which, at such a temperature, are likely to have taken place. (In our experience, such spectra tend to be noisy due to these side reactions). Instead, we chose to estimate the T_G at full cure and the conversion at 350 °C by two alternate methods. First, as noted in the main manuscript, the T_G at full cure for the catalyzed co-network of 50 wt% PT-30 and 50 wt% LECy was 341 °C. For the FlexCy / LECy co-network, the T_G at full cure for the catalyzed and uncatalyzed networks was 316 °C and 340 °C, respectively, a difference of roughly 20 °C due to plasticization of the network by the 2 wt% nonylphenol present in the catalyzed system, which reacts with the cyanate ester intermediates to become “dangling” chain ends. Based on the diBenedetto equation, 2 wt% of free chain ends should depress the T_G by about 20 °C. For BADCy and LECy, T_G depression can also be seen when comparing catalyzed and uncatalyzed networks, but of a smaller magnitude. Thus, a reasonable alternate estimate of the T_G at full cure for the uncatalyzed 50 / 50 PT-30 / LECy co-network is 361 °C. For the extent of conversion by heating to 350 °C, a rough estimate of 97% is obtained by averaging the known values for PT-30 and LECy.

In order to check the validity of these estimates, the diBenedetto equation data generated in Section S4 can be utilized. For the 50 / 50 PT-30 / LECy co-network, using a T_G at full cure of 361 °C and 97% conversion by heating to 350 °C in the DSC yields a root-mean-squared (rms) deviation of 8 °C between observed and predicted values and a reasonable value of 0.40 ± 0.05 for the λ parameter. On the other hand, assuming that 100% conversion is achieved on heating to 350 °C, with a T_G of 354 °C, yields an rms error of 16 °C and a value for λ of 0.32 ± 0.06 . Given that 10 °C is a typical rms error seen in fitting diBenedetto data, and that $\lambda = 0.42 \pm 0.05$ for PT-30 and 0.39 ± 0.06 for LECy, the results assuming 97% conversion are just as expected,

while the results assuming 100% conversion imply a moderately higher error and lower λ value than expected. Furthermore, if a lower conversion of just 94% after heating to 350 °C is assumed, and both the T_G at full cure and λ are allowed to vary (a problematic proposition because the effects of changing these two variables are highly correlated), the best fit is found when the T_G at full cure is 375 °C and $\lambda = 0.46 \pm 0.04$, with an rms error of just 6 °C (with two adjustable parameters instead of one). In addition to the slightly high value for λ , such a solution implies that 1) addition of LECy does not improve the extent of cure at 350 °C despite lowering the T_G and adding flexibility, 2) a substantial 30 °C deviation from the Flory-Fox theory is present (compared to the best estimate presented herein of 15 ± 10 °C), and 3) adding 2 wt% catalyst to the system drops the T_G at full cure by 35 °C. Although these three effects are all possible, none seem likely. Indeed, this final case, along with the previous (100% cured on heating to 350 °C) alternative, are good examples of “marginal” cases, that is, they are just at the limit of what might be reasonable to expect, yet they represent deviations for the T_G at full cure of just -7 °C and +14 °C, respectively, from the “most probable” case. Thus, a value for the T_G at full cure for the 50 wt% PT-30 / 50 wt% LECy co-network of 361 °C, with an uncertainty of ± 10 °C, concisely captures all of these factors.

The values for the T_G at full cure for all networks studied are summarized in Table 1 of the main manuscript. It should be noted that in computing the uncertainties in Table 1, we have made provision for not only the uncertainties in the T_G at full cure, but also for the correlated uncertainties in λ associated with the various assumptions about the extent of cure after heating to 350 °C in the DSC. Particularly for the PT-30 / LECy system, this latter factor increases the uncertainty in the reported conversions to 3-4% from the normal 1-2%.

S3. DSC Data on Rapidly Heated “As Cured” Samples

In previous work,^{S8} we have established that *in-situ* cure represents a significant concern for characterization of the T_G of “as cured” polycyanurate networks, due to their ability to undergo cure below T_G . When cure takes place in the vitreous state, the T_G increases with increasing conversion, in accordance with the diBenedetto equation.^{S6} In more recent work,^{S9} we have established that the rate at which T_G increases may equal or significantly exceed typical heating rates, leading to a situation in which the T_G “runs ahead” of the sample temperature during heating for a significant amount of time. As cure nears completion, the rate of conversion necessarily slows down, allowing the sample temperature to “catch up” to the T_G , at which point the instrument will record the typical signals associated with the transition. Instruments that cannot detect a chemical reaction, such as dynamic mechanical spectrometers, often exhibit signals that are subtle, if present at all, when the T_G “runs ahead” of the sample during heating. As a result, what appears to be a normal measurement of “as cured” T_G may in fact result in an apparent T_G value far above the actual “as cured” T_G .

To avoid these difficulties, it is necessary to utilize a technique such as DSC that will detect the onset of residual cure in a polycyanurate sample. Figures S3-1 and S3-2 compare the DSC and oscillatory TMA scans, at a heating rate of 10 °C / min., of an early batch of FlexCy (precipitated in ethanol rather than isopropanol as with later batches). Kasehagen et al.,^{S10} among others, have noted that the onset of residual cure is often synchronous with T_G in DSC experiments of highly cured polycyanurate samples. In the DSC scan, however, there is a somewhat gradual onset that prevents a precise determination of the T_G . It is clear that residual cure becomes significant at around 250 °C, meaning that during heating the T_G increases significantly due to *in-situ* cure. The corresponding oscillatory TMA in Figure S3-2 shows no

peak in the loss component of stiffness nor a significant decrease in the storage component of the stiffness near 250 °C. Only the step-like change in displacement (actually a kink at the “as cured” T_G which is masked by dimensional changes after the onset of residual cure), a small, broad peak in tan delta, and the increase in the storage component of stiffness provide clues as to the true behavior of the sample. Figure S3-3 shows the same sample scanned at 50 °C / min., a rate that would be expected to preclude significant *in-situ* cure, but does not. The sample under these conditions appears to have two T_G values. Neither T_G value reflects a true “as cured” state.

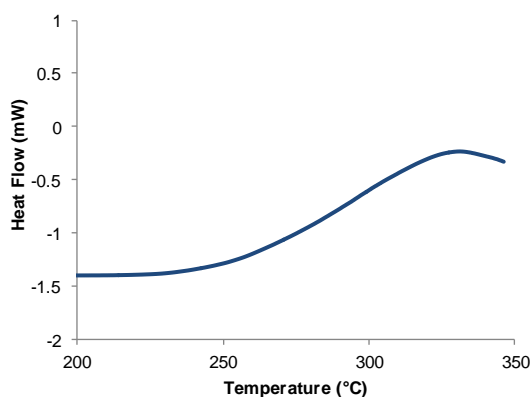


Figure S3-1. DSC scan of FlexCy (precipitated in ethanol) heated at 10 °C / min. after curing for 24 hours at 210 °C.

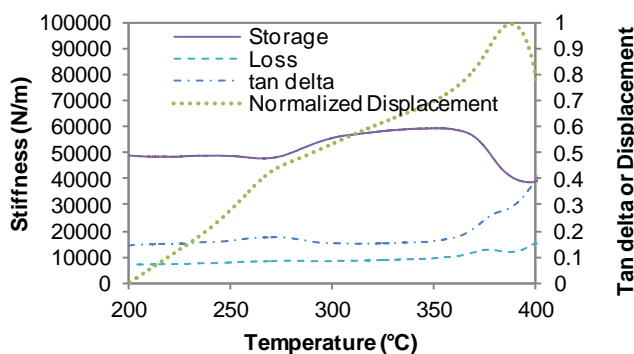


Figure S3-2. Oscillatory TMA scan of FlexCy (same batch as in Figure S3-1) heated at 10 °C / min. after curing for 24 hours at 210 °C.

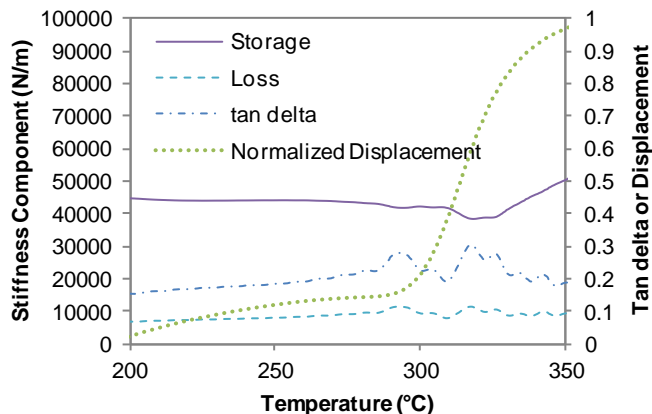


Figure S3-3. Oscillatory TMA scan of FlexCy (same batch as in Figure S3-1) heated at 50 °C / min. after curing for 24 hours at 210 °C.

In previous work,^{S8} we showed that a sufficiently rapid heating rate in oscillatory TMA experiments can reveal the true “as cured” T_G of some polycyanurate samples. However, a further comparison of DSC and oscillatory TMA data at a heating rate of 50 °C / min., shown in Figures S3-4 and S3-5, for uncatalyzed LECy cured for 24 hours at 210 °C, shows that some *in-situ* cure takes place even at this very rapid heating rate. The actual T_G of the sample (250 °C) is, in this case, visible in the DSC trace just at the onset of very rapid heating, while the T_G indicated by TMA is almost 40 °C too high, due to the increase of T_G that accompanies the onset of cure just above 250 °C.

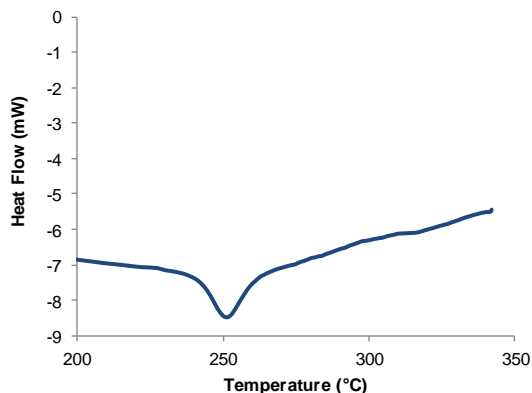


Figure S3-4. DSC scan of uncatalyzed LECy, heated at 50 °C / min. after curing for 24 hours at 210 °C.

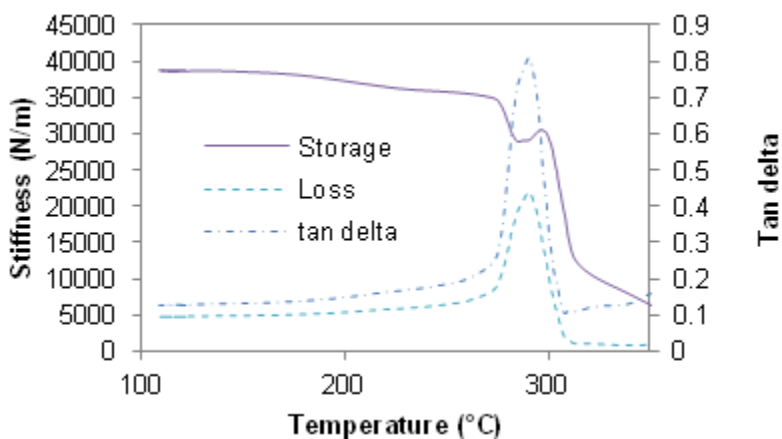


Figure S3-5. Oscillatory TMA scan of uncatalyzed LECy, heated at 50 °C / min. after curing for 24 hours at 210 °C (originally published in Supporting Information of Ref. S1)

In contrast to the DSC scans at the slower heating rate, the onset of cure occurs at a very definite point when the heating rate in the DSC is 50 °C / min. Tests with multiple samples (from the same cured article) show a reproducibility of ± 1 °C for catalyzed LECy when performing DSC scans at 50 °C / min, though, for multiple articles cured using the same nominal protocol, variations of up to 10 °C have been seen. These larger variations among cured articles

using the same nominal protocol likely result from differing degrees of overshoot, or local hot or cold spots in the oven, which expose the articles to slightly different temperatures. Since the T_G of polycyanurate samples is highly dependent on the maximum temperature seen, even for brief periods, these variations in actual temperature translate into variability in T_G when testing multiple articles cured using the same nominal protocol (though not on multiple samples from the same article, assuming the article is small enough to experience a spatially uniform temperature).

Figures S3-6 through S3-9 show the “as cured” DSC scans of PT-30, FlexCy, the 50 / 50 PT-30 / LECy, and the 50 / 50 FlexCy / LECy polycyanurate networks, respectively. From these, the “as cured” T_G (shown in the main manuscript) is inferred from the onset point of residual cure. To date, the rapid DSC technique appears to be the only method that reliably provides an indication of true “as cured” T_G under all circumstances. Using a series of tests with increasing cure temperature, it does appear that the T_G (which is visible below the onset of residual cure if low enough) converges with the onset point of residual cure. If the “as cured” T_G were higher than the onset point by any significant amount, the observed extent of cure (which may be calculated if the residual and total enthalpy of cure are known) would not match the “as cured” T_G if computed via knowledge of the conversion and the diBenedetto equation. A more complete proof of this final point will require additional experiments to validate the apparent baseline for the very rapid DSC measurements, and will be the subject of future work.

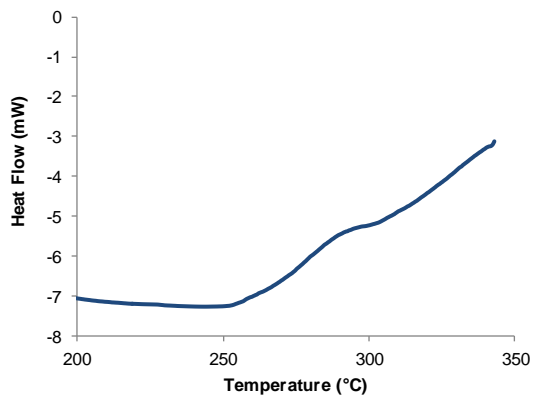


Figure S3-6. DSC scan of uncatalyzed PT-30, heated at 50 °C / min. after 24 hours at 210 °C.

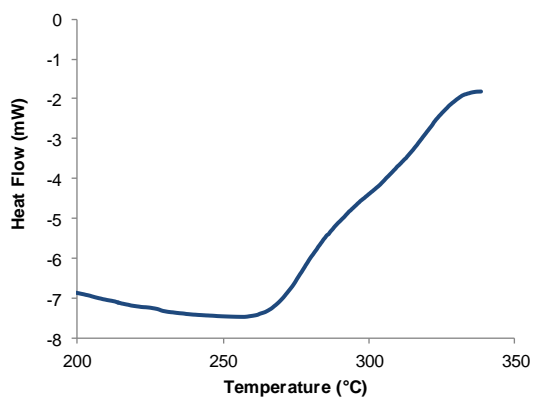


Figure S3-7. DSC scan of uncatalyzed FlexCy, heated at 50 °C / min. after 24 hours at 210 °C.

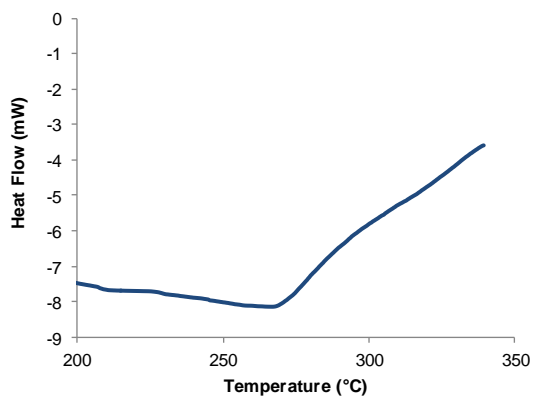


Figure S3-8. DSC scan of uncatalyzed 50 / 50 wt% co-network of PT-30 and LECy, heated at 50 °C / min. after 24 hours at 210 °C.

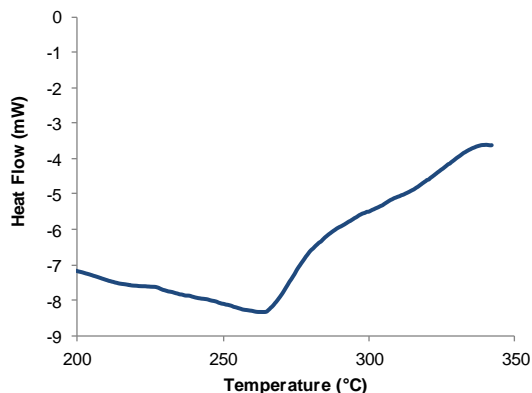


Figure S3-9. DSC scan of uncatalyzed 50 / 50 wt% co-network of FlexCy and LECy, heated at 50 °C / min. after 24 hours at 210 °C.

S4. Determination of diBenedetto equation parameters for polycyanurate networks.

Figures S4-1 through S4-5 provide a graphical illustration of the determination of diBenedetto parameters for the LECy, PT-30, FlexCy, 50 / 50 PT-30 / LECy, and 50 / 50 FlexCy / LECy networks, respectively. Note that we were able to utilize a fairly extensive set of previously collected data on catalyzed LECy^{S11} to aid in the determination, while the co-networks had the least amount of available data. The diBenedetto equation, which is

$$\frac{(T_G - T_{G0})}{(T_{G\infty} - T_{G0})} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (\text{S4-1})$$

contains three parameters, the T_G of uncured monomer (T_{G0}), the T_G at full cure ($T_{G\infty}$), and the (essentially empirical) fitting parameter λ . In Eq. S4-1, α represents the conversion. As in previous work, T_{G0} was estimated by a separate DSC scan and is readily observed. The calculation of $T_{G\infty}$ involved modulated DSC, with techniques such as oscillatory TMA and a knowledge of the likely value of λ evaluated as supporting evidence. These procedures are described in detail in Section S2. In the case of all networks except the 50 / 50 PT-30 / LECy

system, the only parameter determined by a fit of data in which DSC is used to simultaneously measure conversion and T_G (via onset of residual cure if necessary) is λ .

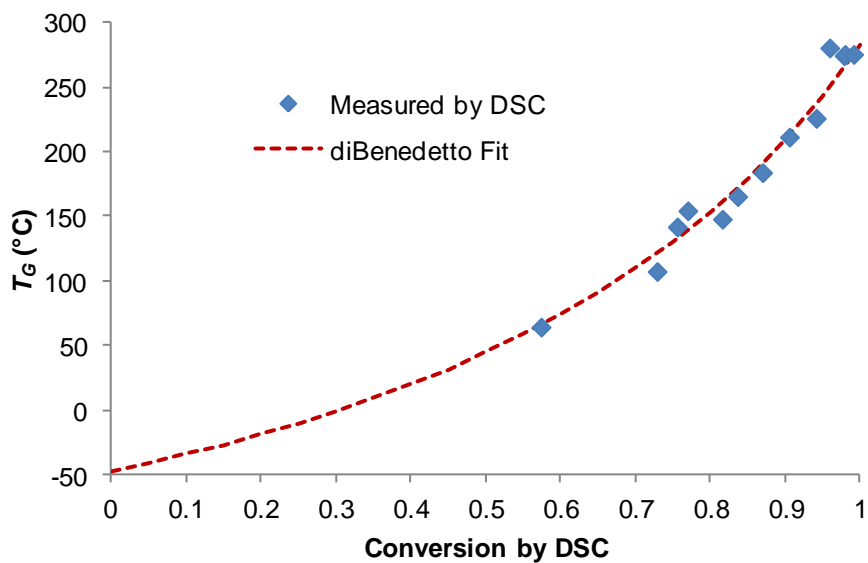


Figure S4-1. diBenedetto equation fit for LECy (data for catalyzed system with 2 phr 30:1 nonylphenol : Cu(II)-acetylacetonate, 160 ppm Cu).

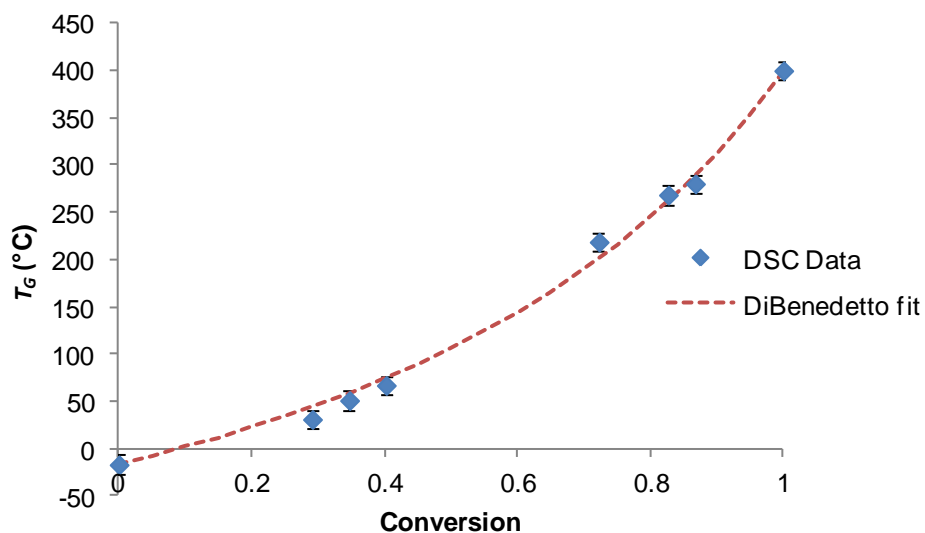


Figure S4-2. diBenedetto equation fit for PT-30 (uncatalyzed)

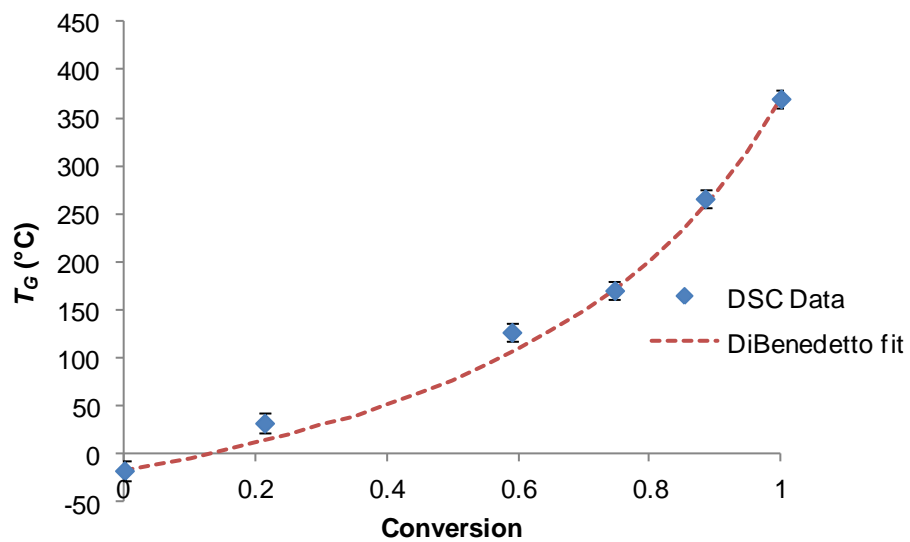


Figure S4-3. diBenedetto equation fit for FlexCy (uncatalyzed).

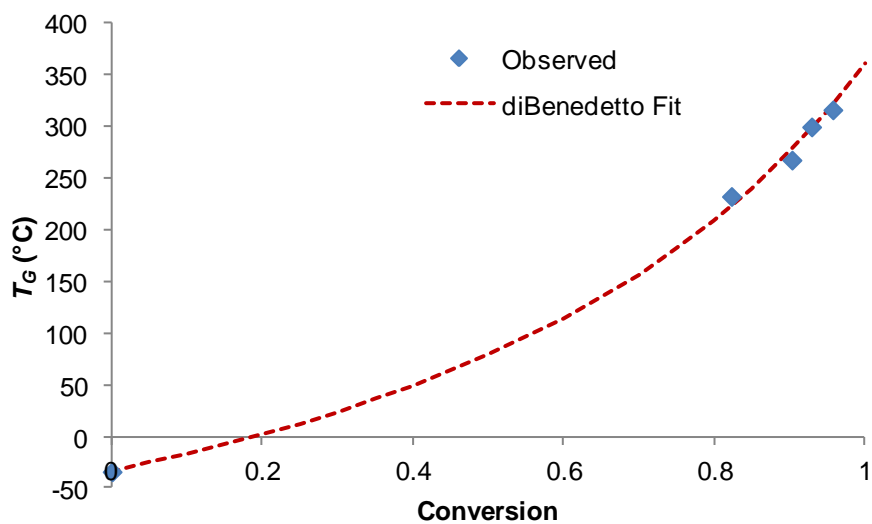


Figure S4-4. diBenedetto equation fit for 50 / 50 PT-30 / LECy (uncatalyzed).

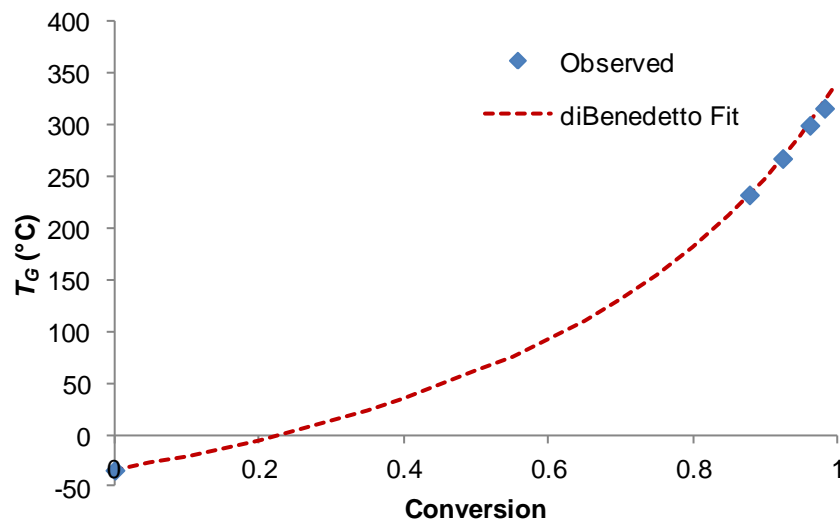


Figure S4-5. diBenedetto equation fit for 50 / 50 FlexCy / LECy (uncatalyzed).

These single parameter fits were determined by measuring the sum of squared residuals for values of λ at intervals of 0.01 and noting the value which the sum of squared residuals was minimized. In these cases, the sum of squared residuals shows a straightforward quadratic dependence on λ , with a clear single minimum. The error bounds were determined by noting the values of λ for which a χ^2 parameter (per degree of freedom) increased by one. The χ^2 parameter was taken as sum of normalized residuals squared, where normalized residuals were determined by dividing the residual by a standard deviation of either 10 °C, which is typical for these experiments, or the average absolute deviation for the best fit, whichever was smaller. The appropriateness of this procedure was checked by examining a plot of predicted and observed T_G values as a function of conversion. It was noted that when λ was varied by an amount equal to the uncertainty, a systematic lack of fit typically was just apparent, whereas variation by more than the uncertainty produced a clear lack of fit. The method for calculating the uncertainty parameter thus appears to represent a reasonable approach. Note also that the extra data

available for the single-component networks does not noticeably improve the fit, although it does provide some additional confidence for the validity of the equation at lower T_G values. Because the current study does not involve these lower values, the more limited data for the co-networks is sufficient for the purposes of the study.

For the PT-30 / LECy network, a single parameter fit was performed using the most probable T_{G0} and $T_{G\infty}$ values, as with the other networks. However, as mentioned in Section S2, there is additional uncertainty surrounding the extent of cure in samples heated to 350 °C for this network. Note that this extent of cure parameter must be taken into account when computing conversions based on residual heating in the DSC, as done for this study. As mentioned in Section S2, additional fits were performed on this network in order to help validate the most probable value for $T_{G\infty}$. In one case, a fit was performed for λ using the lowest reasonable value for $T_{G\infty}$ and a conversion of 100% at the end of DSC heating, for comparison. In addition, a multi-parameter fit in which $T_{G\infty}$ and λ were simultaneously varied while assuming the lowest reasonable value for conversion at the end of DSC heating was also performed. This type of fit may be problematic due to a strong correlation between the value of $T_{G\infty}$ and λ when minimizing residuals, however, in this particular case, there was a single, clear global minimum in the sum of squared residuals with reasonable parameter values and no unusual behavior, so the results in this particular case were considered reliable. In this case, the known value of conversion on heating to 350 °C acts in combination with the curvature inherent in the conversion versus T_G curve to effectively constrain both $T_{G\infty}$ and λ simultaneously. These three different fits using different assumptions for the extent of conversion and $T_{G\infty}$ parameters all produce slightly different “best fit” values for λ . Thus, when reporting the final uncertainty in λ in Table 1 in the main manuscript, we have increased the uncertainty in order to cover the range of values

produced by all fits (each with its own uncertainty interval), rather than relying on any one of the fits performed.

Finally, it should be noted that for the LECy system, the value of λ is derived from data on the catalyzed system, and assumed to be the same for the uncatalyzed system (with different values, specific to the uncatalyzed system, for $T_{G\infty}$ and T_{G0}). T_{G0} for LECy is identical within experimental error for catalyzed and uncatalyzed systems. The equality of the value of λ for both catalyzed and uncatalyzed systems is consistent with the theory underlying the diBenedetto equation, as well as the known insensitivity of λ to cyanate ester network type.

S5. Figure 1 from Ref. 36 in the main manuscript (same as Ref. S2 below)

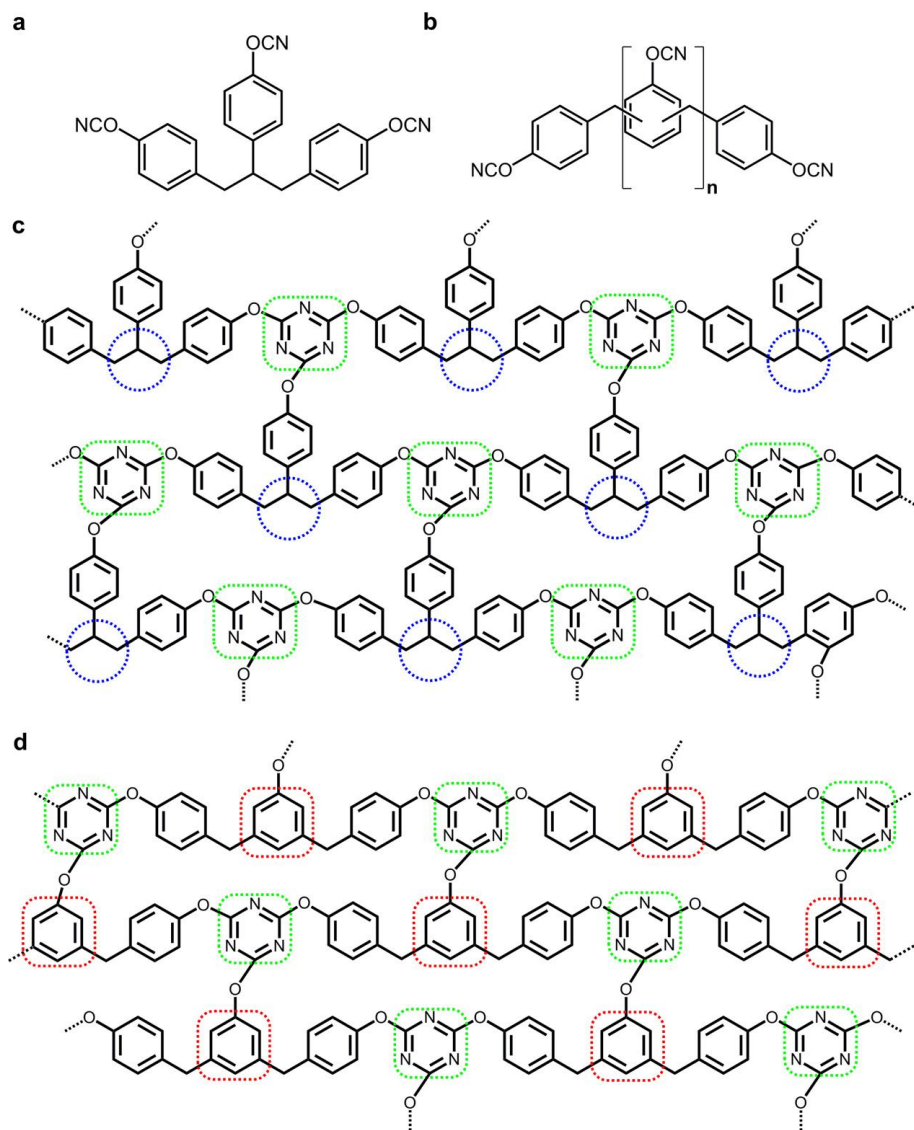


Figure S5-1. a) Chemical structure of FlexCy compared with b) approximate chemical structure ($n \sim 1$) for Primaset_ PT-30 resin c) after cure, the idealized network architecture of FlexCy features a “checkerboard” pattern of relatively flexible trisubstituted propyl junctions (dashed circles) alternating with more rigid triazine ring junctions (dashed rounded rectangles), d) whereas in PT-30 (shown with $n = 1$ for convenience), the network architecture features only rigid triazine ring or phenyl ring junctions.

References

- S1. Davis, M. C.; Guenther, A. J.; Groshens, T. J.; Reams, J. T.; Mabry, J. M., *J. Polym. Sci. Part A, Polym. Chem.* **2012**, *50*, 4127-4136.
- S2. Guenther, A. J.; Davis, M. C.; Lamison, K. R.; Yandek, G. R.; Cambrea, L. R.; Groshens, T. J.; Baldwin, L. C.; Mabry, J. M. *Polymer* **2011**, *52*, 3933-3942.
- S3. Guenther, A. J.; Davis, M. C.; Ford, M. D.; Reams, J. T.; Groshens, T. J.; Baldwin, L. C.; Lubin, L. M.; Mabry, J. M. *Macromolecules* **2012**, *45*, 9707-9718.
- S4. Marella, V. V. An Investigation on the Hydrolysis of Polyphenolic Cyanate Esters using Near-IR Spectroscopy. M. S. Thesis, Drexel University, Philadelphia, PA, 2008.
- S5. Guenther, A. J.; Lamison, K. R.; Davis, M. C.; Cambrea, L. R.; Yandek, G. R.; Mabry, J. M. In *Cure Characteristics of Tricyanate Ester High-Temperature Composite Resins*, 2011 SAMPE Spring Technical Conference and Exhibition - State of the Industry: Advanced Materials, Applications, and Processing Technology, Long Beach, CA, SAMPE International Business Office: Long Beach, CA, 2011; paper 56-1681.
- S6. Pascault, J. P.; Williams, R. J. J. *J. Polym. Sci. Part B Polym. Phys.* **1990**, *28*, 85-95.
- S7. Guenther, A. J.; Lamison, K. R.; Vij, V.; Reams, J. T.; Yandek, G. R.; Mabry, J. M. *Macromolecules* **2012**, *45*, 211-220.
- S8. Guenther, A. J.; Lamison, K. R.; Yandek, G. R.; Masurat, K. C.; Reams, J. T.; Cambrea, L. R.; Mabry, J. M., Role of concurrent chemical and physical processes in determining the maximum use temperatures of thermosetting polymers for aerospace applications. In *Abstr. Pap. Am. Chem. Soc.* **2011**, (243rd ACS National Meeting & Exposition, Denver, CO, 2011), POLY-262.
- S9. Guenther, A. J.; Reams, J. T., Sahagun, C. M.; Davis, M. C.; Mabry, J. M. in *Post-Vitrification Cure Kinetics of High-Temperature Composite Resins: Implications for Characterization and Performance*, 2013 SAMPE Spring Technical Conference and Exhibition - Education & Green Sky – Materials Technology for a Better World, Long Beach, CA, SAMPE International Business Office: Long Beach, CA, 2013; in press.
- S10. Kasehagen, L. J.; Haury, I.; Macosko, C. W.; Shimp, D. A. *J. Appl. Polym. Sci.* **1997**, *64*, 107-113.
- S11. Reams, J. T.; Guenther, A. J.; Lamison, K. R.; Vij, V.; Lubin, L. M.; Mabry, J. M. *ACS Appl. Mater. Interfaces* **2012**, *4*, 527-535.