

# Thermally Controlled Molecular Disassembly of a Crosslinked Polymer Network by the Incorporation of Sterically Hindered Urea Linkages

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**ABSTRACT:** Crosslinked polymer networks are excellent materials for multiple applications. However, although their crosslinked structure gives them many positive attributes, it also makes them intractable. Therefore, it is exceedingly difficult to reprocess crosslinked networks without exposure to extreme degradation conditions. In this work, we were able to create a crosslinked network that showed controlled disassembly upon stimulus. It was found that a controlled network disassembly process could be invoked by the incorporation of sterically hindered urea linkages into the polymer network. The network was shown to disassemble upon exposure to heat, whereas in the absence of heat, the network was found to maintain its crosslinked structure. The disassembly temperature could be varied by careful selection of the cleaving agent. This work focuses on showing the controlled network disassembly of a crosslinked polymer matrix as a function of temperature. Herein, we describe the factors that control the disassembly temperature and conclude with a possible mechanism for the disassembly process. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 856–864, 2002

**Key words:** adhesives; degradation; networks; thermal properties; thermosets

## INTRODUCTION

Griffith first coined the term command-destruct to describe the concept of reworkable materials.<sup>1</sup> In Griffith's view, reworkability could be imparted into any system that incorporated a means to molecularly disassemble the polymer network. Currently, most thermosets are intractable, which gives them longevity in strength, making them the material of choice.<sup>2–8</sup> However, smart materials that decrosslink on command allow removal of any number of components from one another that are embedded or bonded together by the polymer matrix.<sup>2,3,4</sup> Furthermore, there are

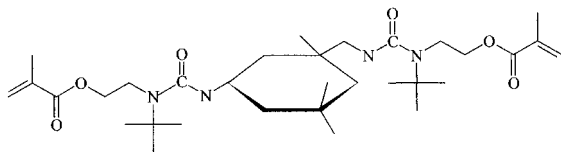
also environmental issues that a reworkable system addresses.<sup>5</sup> Therefore, if a material could be designed for disassembly on a molecular scale, many of the disadvantages of crosslinked networks can be addressed without losing the positive attributes of the thermosets. Although researchers have tried a variety of approaches to date,<sup>4,9–24</sup> no one ideal method exists to impart reworkability into any polymer system. Moreover, although a great deal of work was reported for reworkable epoxy-based systems, none were reported using acrylates. Acrylates do present some advantages over other systems, such as speed of cure and other considerations.<sup>25</sup>

Velankar et al.<sup>25</sup> demonstrated that UV curable methacrylates with sterically hindered urea linkages could be made. Moreover, they showed that the sterically hindered urea linkages were

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## Synthesis

*t*-BAEM-IPDI-*t*-BAEM

**Figure 1** *t*-BAEM-IPDI-*t*-BAEM.

susceptible to attack by basic species, which they used to take polymer linkages from one network and sever and simultaneously form linkages with another polymer network to form interpenetrating networks that exhibited useful modulus changes. We hypothesized that one could take this same reaction and use it to create a reworkable matrix by incorporating the same sterically hindered urea linkages within the network and, rather than sever and reconnect the linkages to another matrix, it could be possible just to sever the bond, and hence, decrosslink the network. To determine the structure of the crosslinker, we returned to the structure in Velankar et al.'s original article and focused on the critical structural elements for the creation of the reworkable crosslinker. The critical elements in Velankar et al.'s article were the two sterically hindered urea linkages. The simplest way to incorporate the two urea linkages was to react two *tert*-butyl(aminooethyl) methacrylate (*t*-BAEM) units with isophorone diisocyanate (IPDI) directly, ignoring the reaction step Velankar et al. used to incorporate a polymer backbone into their crosslinker because we were not interested in making an interpenetrating network, which was the focus of their study. Furthermore, Velankar et al. showed that these types of molecules could be crosslinked upon exposure to UV radiation with the photoinitiator 2,2-diethoxyacetophenone (DEAP). Therefore, DEAP was also used in this study.

In each novel crosslinker (Figure 1), we describe the incorporation, via synthesis, of two sterically hindered, hence cleavable, urea linkages that would cause the polymer matrix to disassemble upon command. To facilitate breaking down the matrix, we would add a basic species to attack the sterically hindered urea linkages. However, whereas Velankar et al. used a chain extender (dibasic species) that could react with two sterically hindered urea linkages, and upon repeating this reaction form block copolymers, we propose an attacking base that could only react

once. Moreover, the molar equivalent of the attacking species would equal the molar equivalent of the number of reworkable linkages that are present within the matrix. Therefore, upon heating, each basic species would then attack every sterically hindered urea linkage. As all of the urea linkages are severed, the matrix will then be a series of linear polymer chains (formally the backbone of the matrix) and smaller segments made from the crosslinker fragments. Hence, the matrix has undergone its thermally controlled molecular disassembly process.

However, we also wanted to take Velankar et al.'s original idea further. Velankar et al. stated in their article that the steric hindrance caused by the *t*-butyl group resulted in a weakening of the urea linkage, making it susceptible to thermal cleavage. It seems plausible that if this cleaving reaction were a function of steric hindrance of the urea linkage, then the steric hindrance of the cleaving agent would also have an effect. If the steric nature of the cleaving agent did have an effect on the cleaving temperature, then this could also allow us to tune in a decrosslinking temperature. Therefore, it would be conceivable that any reworkable temperature could be possible by finding the appropriate cleaving agent with a specific steric nature. On the basis of these requirements, four amines were chosen to test the steric hindrance hypothesis: *n*-dibutylamine, diisobutylamine, diisobutylamine, and bis(2-ethylhexyl)amine. The first three amines are all structural isomers of one another and increase in steric hindrance around the amino group as you move from left to right. We also wished to determine the effects of the basicity of the cleaving species; therefore, two alcohols, 1-hexanol and 1-nonanol, were also chosen as cleaving agents because it is proposed that the severing of the sterically hindered urea linkage is also dependent on, in part, the basic strength of the attacking species.

## EXPERIMENTAL

### Materials

All of the fine chemicals were purchased from the Aldrich Chemical Co. (NJ, USA) and used without further purification. HPLC-grade solvents from Aldrich were used with activated molecular sieves overnight for drying. The solvents were used without further purification.

**Table I** Components for Each Prepolymer Matrix of *t*-BAEM-IPDI-*t*-BAEM

Sample	Prepolymer (g)	Reworkable Bonds (mol)	Added Component (g)	Added Component (mol)
Control	2.31	4.62E-03	0.00	0.00E+00
Hexane	3.71	7.43E-03	0.64	7.43E-03
Toluene	3.97	7.95E-03	0.73	7.92E-03
Hexanol	4.26	8.53E-03	0.88	8.61E-03
Nonanol	6.11	1.22E-02	1.94	1.34E-02
<i>n</i> -Butylamine	3.46	6.93E-03	0.90	6.96E-03
Diisobutylamine	3.45	6.91E-03	0.89	6.89E-03
Diisobutylamine	4.07	8.15E-03	1.04	8.05E-03
<i>bis</i> (2-Ethylhexyl)amine	4.03	8.07E-03	1.93	7.99E-03

### Instruments

<sup>1</sup>H-NMR spectra were taken on a Bruker AC-250 NMR spectrometer. Infrared spectra were taken on a Bio-Rad Excalibur Series FTS 3000. A thermal analysis instrument TGA 2050 thermogravimetric analyzer under nitrogen was used for the thermal analysis.

### Synthesis

A dry 250-mL round-bottom flask was equipped with a stir bar and a rubber septum and charged with argon. To the flask were added 48.95 g (0.22 mol) of isobornyl methacrylate (tech grade) and 45.80 g (0.25 mol) of *t*-BAEM. Stirring was initiated and 27.47 g (0.12 mol) IPDI was added. After 2 h, 1% by weight (1.23 g, 0.0060 mol) of DEAP as the photoinitiator was added. The prepolymer was further stirred for 1 h and then the monobasic species was added as described in the Results and Discussion section.

For the <sup>1</sup>H-NMR sample, HPLC-grade toluene was substituted for the isobornyl methacrylate and the same procedure was used. A rotary evaporator was used to remove excess toluene (toluene was observed in the <sup>1</sup>H-NMR). A complex splitting pattern was observed for the *t*-BAEM-IPDI-*t*-BAEM molecule. This occurs for two reasons. First, *t*-BAEM-IPDI-*t*-BAEM is a nonsymmetrical molecule because IPDI has a nonsymmetrical structure. Therefore, the two terminal *t*-BAEM groups experience nonequivalent chemical environments. Second, IPDI is received as a mixture of isomers that further increases the nonequivalent chemical environments experienced by the protons of *t*-BAEM-IPDI-*t*-BAEM. Hence, higher ordered coupling effects were seen in the <sup>1</sup>H-NMR spectrum.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, in ppm) δ: 6.20 (s, 2H, H<sub>a</sub>-C=), 5.70 (s, 2H, H<sub>b</sub>-C=), 5.55 (m, 1H, -CO-NH-CH-), 5.25

(t, 1H, -CO-NH-CH<sub>2</sub>-), 4.28 (complex, 4H, -CH<sub>2</sub>-O-), 4.05 (triplets of triplets, 1H, -NH-CH-), 3.53 (complex, 4H, -CH<sub>2</sub>-N(C(CH<sub>3</sub>)<sub>3</sub>)-), 3.07 (d, 2H, -CH<sub>2</sub>-NH-CO-), 2.02 (s, 6H, =C(CH<sub>3</sub>)-), 1.85-1.73 (complex, 2H, IPDI), 1.49 (s, 18H, -C(CH<sub>3</sub>)<sub>3</sub>), 1.4-0.9 (complex, 15H, IPDI).

IR (Neat, in cm<sup>-1</sup>): 3404 (medium, R<sub>2</sub>NH), 3095 (very weak, =CH<sub>2</sub>) 2957 (strong, CH), 1714 (very strong, C=O), 1655 (very strong, C=O), 1521 (strong, N-H), 1496 (strong, N-H), 1455 (medium, CH), 1392 (medium, CH), 1362 (strong, C-N), 1338 (strong, C-N), 1296 (strong, C-N), 1205 (medium, C-O), 1163 (strong, C-O), 1012 (weak, C-C), 942 (medium, =CH<sub>2</sub>), 815 (weak, C-C), 770 (weak, C-C), 731 (weak, C-C), 695 (weak, C-C), 652 (weak, C-C).

### Extraction Protocol

This standard protocol was used to study the decrosslinking behavior of the networks after the disassembly process. The sample was prepared by adding all of the components together as described in Table I. The matrix was then cured by exposure to UV radiation (Fusion UV Systems Inc., controlled by a P300M power supply fitted with a D bulb, λ = 190-360 nm, 20,000 mJ/cm<sup>2</sup>). To a 15-mL vial was added a carefully determined amount of the polymer matrix. The weight of this sample was noted; the glass vial was sealed and placed into a specific temperature environment. After exactly 1 h, the vial was removed from the oven and allowed to cool for 1 h at room temperature. HPLC-grade toluene was then added to the sample with the amount noted. The sealed samples were then allowed to sit in the toluene overnight.

The following morning, a Whatman Grade 4 piece of filter paper was weighed and the weight was recorded. The filter paper was then placed in a Büchner funnel, which was then placed into a

heavy-wall side-arm filter flask attached to a fitted vacuum pump. The glass vial was then opened and the contents of the vial were placed on the filter paper. The liquid portion was pulled through the filter paper under suction. The glass vial was washed with excess HPLC-grade toluene and this toluene was also placed on the filter paper. Any excess solid or residue on the filter paper was washed with fresh toluene. The filter paper, including any solid present on it, was then allowed to dry under suction. The filter paper and any solid present were then removed from the funnel and placed in a 150°C oven for 3 h to thoroughly remove any excess toluene and other volatiles. The filter paper and dried solid was then allowed to sit at room temperature overnight, which allowed the filter paper and the polymer matrix to come to equilibrium with the ambient environment. The next morning, the filter paper was weighed and its weight was recorded. The amount of decrosslinking was determined, which was described as a percentage of the gel fraction remaining on the filter paper to the amount of polymer sample originally used.

#### Procedure for Refluxing *t*-BAEM-IPDI-*t*-BAEM in the Presence of Amines to Study the Decrosslinking Mechanism

A dry 250-mL round-bottom flask was equipped with a stir bar and a rubber septum and charged with argon. Dry, HPLC-grade toluene (17.84 g) and 19.15 g (0.088 mol) isophorone diisocyanate were added and the mixture was stirred. *t*-BAEM (31.98 g; 0.17 mol) was then added and the reaction was allowed to stir overnight. The reaction was then split into two equal portions [34.15 g (49.51%) and 34.82 g (50.49%)]. Two equivalents of bis(2-ethylhexyl)amine (21.00 g, 0.087 mol) and diisobutylamine (11.02 g, 0.085 mol) were added to each reaction vessel, respectively. The reaction vessels were placed in a 125°C oil bath and refluxed for 48 h. Excess toluene was then rotary evaporated off. A white solid residue remained for the bis(2-ethylhexyl)amine sample and the diisobutylamine sample produced a thick orange oil. <sup>1</sup>H-NMR spectra were collected and will be discussed in the Results and Discussion section.

## RESULTS AND DISCUSSION

### Investigation of the Reworkable Matrix

*t*-BAEM-IPDI-*t*-BAEM matrix is proposed to convert from a three-dimensional network to a series of linear polymers. Three-dimensional networks, because of their inherent matrix structure, will fail to dissolve in any nondegrading solvent. Linear chains, providing that the solvent is not a poor solvent, will dissolve. To quantify, the extent of decrosslinking, the extraction protocol described in the Experimental section, was performed to separate any dissolvable components from the rest of the network.

The *t*-BAEM-IPDI-*t*-BEAM was prepared as stated above in the Experimental section with the total solution weight being 123.45 g. The amount of reworkable crosslinker formed was 73.27 g. Therefore, in a 1-g sample, 0.59 g of crosslinker was present per gram of solution (73.27/123.45). Therefore, in a 1-g sample,  $1.00 \times 10^{-3}$  mol of crosslinker per gram exist (MW crosslinker is 592.83 g/mol). Two moles of basic species are needed because each crosslinker contains two reworkable units. Therefore,  $2.00 \times 10^{-3}$  mol of the basic species per gram of prepolymer solution are needed. The polymer solutions in Table I were prepared by the addition of a known amount of the *t*-BAEM-IPDI-*t*-BEAM prepolymer solution to another component. As Table I shows, the moles of the added component equal the moles of the reworkable bonds present in the *t*-BAEM-IPDI-*t*-BEAM prepolymer solution.

Table II provides the weights of each sample that was placed in the vials that underwent the extraction protocol and the oven temperature for each of the samples.

Following the extraction work up, Table III provides the percentage of the original polymer sample that remained on the filter paper. Table III shows that the column with the first set of vials, which was maintained at room temperature, has experimental values considerably below 100% except the control sample. This occurred because these matrices have yet to undergo the decrosslinking process. Therefore, the nonreactive components (hexane, toluene, alcohols, or amines) are still present within the matrix, except in the control sample. Moreover, these nonreactive diluents will be washed away from the polymer network during the extraction protocol. Table III shows the percentage of nonreactive fraction present in each sample.

**Table II Weight of Polymer Samples Placed into Four Numbered Vials (in g) and Vial Temperature Environments (°C)**

Sample	Vial 1 (g)	Vial 1 (°C)	Vial 2 (g)	Vial 2 (°C)	Vial 3 (g)	Vial 3 (°C)	Vial 4 (g)	Vial 4 (°C)
Control	0.4109	25	0.5476	125	0.1658	150	0.1600	170
Hexane	0.3626	25	0.4514	125	0.3093	150	0.3193	170
Toluene	0.5895	25	0.3582	125	0.3911	150	0.2069	170
Hexanol	0.3631	25	0.5330	125	0.3747	150	0.3434	170
Nonanol	0.4258	25	0.4177	125	0.4810	150	0.6332	170
<i>n</i> -Butylamine	0.5852	25	0.4992	60	0.4624	80	0.5170	125
Diisobutylamine	0.3973	25	0.4988	60	0.5678	80	0.5306	125
Disecbutylamine	0.3428	25	0.4443	60	0.4805	80	0.3886	125
<i>bis</i> (2-Ethylhexyl)amine	0.3463	25	0.4746	60	0.5107	80	0.6697	125

Table III shows that the extraction studies using the control, toluene, and hexane samples show no detectable decrosslinking behavior up to 170°C. Both alcohols decrosslink the network. As shown in Figure 2, significant decrosslinking occurs at temperatures in excess of 150°C. Moreover, both alcohols are equally reactive to the decrosslinking process as a function of temperature. Figure 2 also shows the extraction studies in the presence of amines. All the amines show complete decrosslinking by 120°C. This suggests that the amines are more reactive than the alcohols to decrosslinking the *t*-BAEM-IPDI-*t*-BAEM matrix. This shows that the severing of the sterically hindered urea linkages is dependent on, in part, the basic strength of the attacking species. After disassembly with the alcohol and the amine cleaving agents, the samples were found to be flowable liquid samples.

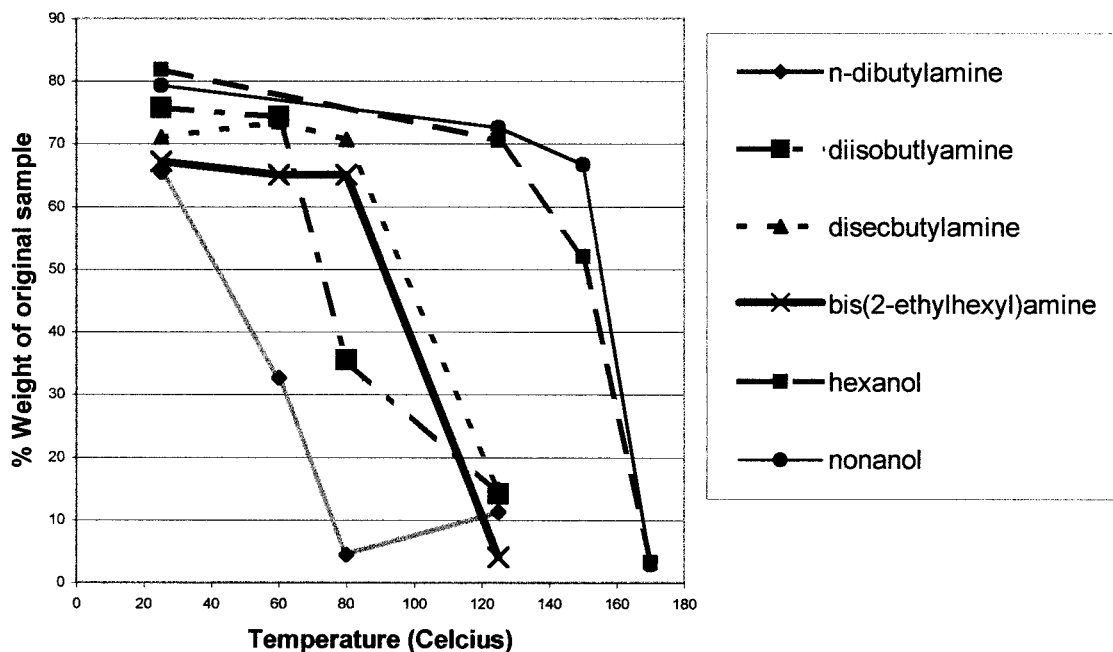
Figure 2 shows that the *n*-dibutylamine is the most reactive amine, showing almost complete decrosslinking by 80°C. This is followed by di-

isobutylamine. Finally, disecbutylamine and *bis*(2-ethylhexyl)amine show similar behavior. The results show that for the three dibutylamine structural isomers as the steric hindrance around the amine site increases, the decrosslinking temperature also increases. The data suggest that basic strength followed by steric hindrance of the cleaving species determine the disassembly temperature. Table IV gives the network disassembly temperature, which for this study is defined as the temperature where 50% of the network was degraded as determined by extractable content. So for the *n*-dibutylamine sample, the vial 1 sample initially was 65.46% (Table III); therefore, the temperature from Figure 2 corresponding to 32.73% was found to be at 60°C. On the basis of this data, the decrosslinking temperature and the reactivity order for all of cleaving agents can be determined.

The extraction studies show that disassembly is occurring on a molecular level. The experiments show that a basic species can sever the

**Table III Amount of Polymer Samples Remaining on Filter Paper Converted as Percentage of Original Samples**

Sample	Vial 1 (%)	Vial 2 (%)	Vial 3 (%)	Vial 4 (%)	Nonreactive Fraction (%)
Control	99.08	99.29	102.71	97.38	0.00
Hexane	90.18	90.03	93.86	89.98	14.71
Toluene	84.87	85.23	90.97	83.42	15.53
Hexanol	81.85	70.54	52.04	3.26	17.12
Nonanol	79.33	72.56	66.74	2.89	24.10
<i>n</i> -Butylamine	65.46	32.65	4.43	11.28	20.64
Diisobutylamine	75.74	74.34	35.56	14.19	20.51
Disecbutylamine	71.03	73.49	70.66	14.82	20.35
<i>bis</i> (2-Ethylhexyl)amine	67.17	65.02	65.01	4.06	32.38



**Figure 2** Extraction studies of *t*-BAEM-IPDI-*t*-BAEM using 2 equiv of alcohol and amine severing agents.

sterically hindered urea linkages, converting a crosslinked network into a series of linear chains. These experiments also show that the decrosslinking reaction is controllable, depending on the basic nature and the sterics of the cleaving species. Hence, this suggests that one would be able to select the decrosslinking temperature by choosing an appropriate attacking species.

#### Effect of Varying the Equivalents of the Added Component Versus the Equivalents of Reworkable Linkages

When the moles of sterically hindered urea linkages equaled the moles of the severing agent, then the matrix could be disassembled. However, to sever each crosslinker, only one of the sterically hindered urea bonds needs to be severed on each crosslinker. Therefore, it could be possible for less than a molar equivalent of cleaving agent, compared to the moles of reworkable urea linkages, to be used and still decrosslink the matrix. This idea was investigated using 1 equiv and 1.5 equiv of decrosslinking species (versus the 2 equiv of sterically hindered urea linkages present with the matrix). The solutions were prepared and the decrosslinking behavior was determined in a similar manner as described above. The toluene and the hexane samples with 1 and 1.5 equiv were

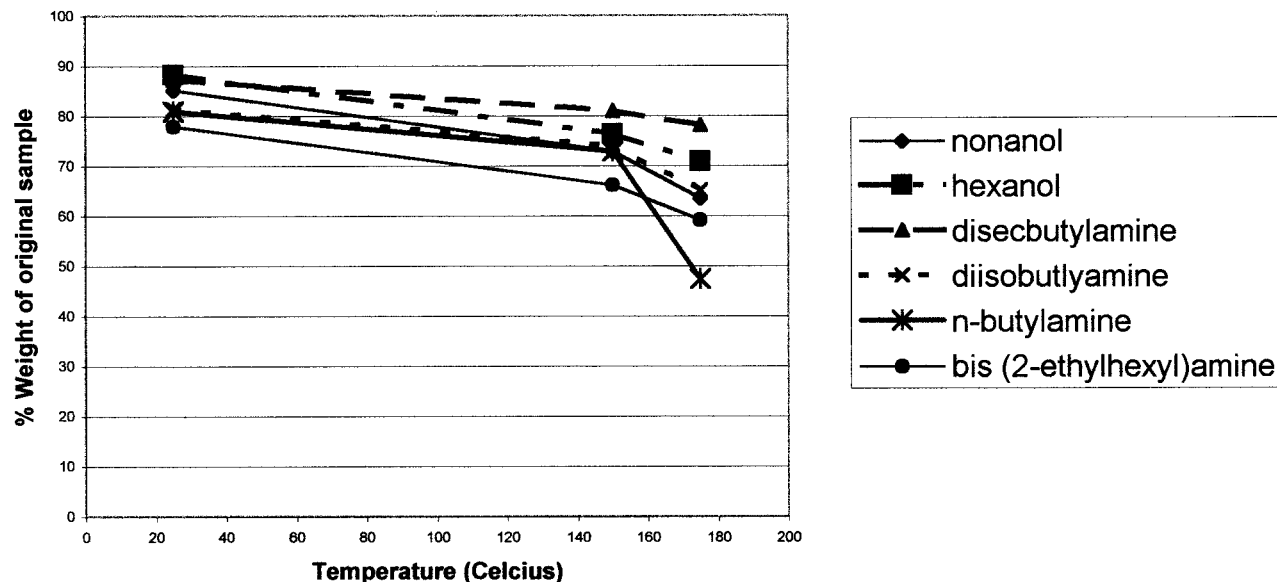
omitted because these did not decrosslink the network. These results are expected considering the absence of decrosslinking seen in the 2 equiv toluene and hexane samples described above.

For the 1 equiv system, Figure 3 provides the data in the presence of alcohols and amines. For the alcohols, some decrosslinking as a function of temperature is seen but not the complete decrosslinking reaction shown when 2 equiv of alcohols are used. *n*-Dibutylamine shows some decrosslinking, whereas diisobutylamine, bis(2-ethylhexyl)amine, and diisobutylamine show no significant decrosslinking.

For the 1.5 equiv system, Figure 4 shows that the alcohols show some decrosslinking as a

**Table IV** Disassembly Temperature Behavior for *t*-BAEM-IPDI-*t*-BAEM when Exposed to Various Bases

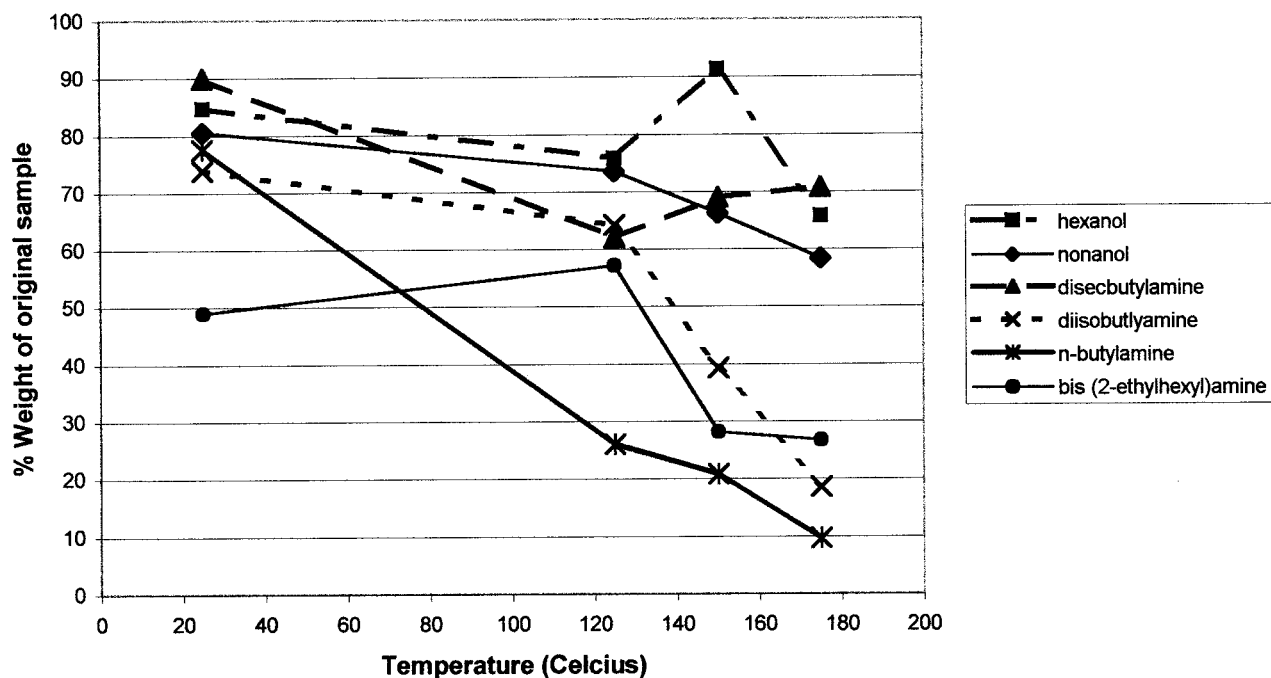
Cleaving Species	Temperature of 50% Disassembly (°C)
<i>n</i> -Dibutylamine	60
Diisobutylamine	79
<i>bis</i> (2-Ethylhexyl)amine	98
Diisobutylamine	108
Hexanol	155
Nonanol	159



**Figure 3** Extraction of *t*-BAEM-IPDI-*t*-BAEM using 1 equiv of alcohol and amine cleaving agents.

function of temperature but again not the complete decrosslinking shown when 2 equiv of alcohols are used. Figure 4 also shows that 1.5 equiv of amines decrosslinks the network as a function of temperature. The *n*-dibutylamine, diisobutylamine, and bis(2-ethylhexyl)amine

show almost complete decrosslinking, whereas the diisobutylamine does not decrosslink the matrix. This data is consistent with the idea that factors dictated by base strength and sterics play a considerable controlling disassembly.



**Figure 4** Extraction of *t*-BAEM-IPDI-*t*-BAEM using 1.5 equiv of alcohol and amine cleaving agents.

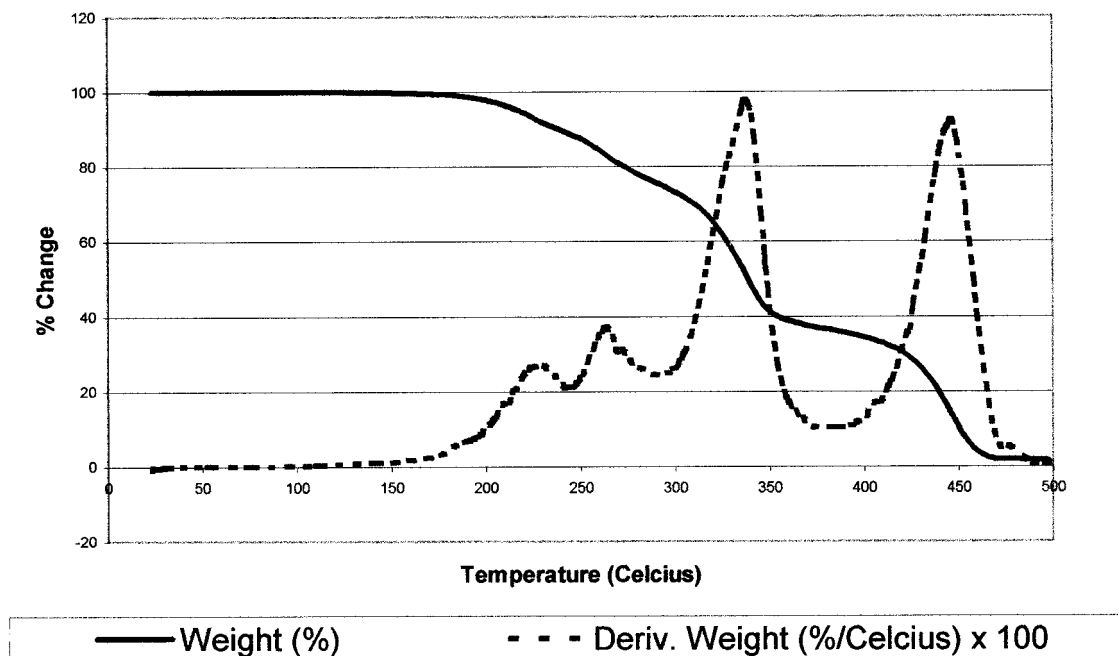


Figure 5 TGA of *t*-BAEM-IPDI-*t*-BAEM.

#### Thermogravimetric Analysis of the *t*-BAEM-IPDI-*t*-BAEM Matrix

This network disassembles in the presence of alcohols and amines but no evidence was provided, suggesting that the network is not undergoing thermal degradation because of its inherent thermal degradation. Figure 5 shows the TGA curve and the first derivative curve of weight loss with respect to temperature of a cured sample *t*-BAEM-IPDI-*t*-BAEM with no other species present. Four transitions are seen at 227, 263, 336, and 446°C. On the basis of the previous studies and the thermal degradation behavior, it is concluded that thermal degradation up to 175°C does not play a significant role in decrosslinking the network in the temperature ranges considered in this study.

#### Investigation of the Reworkable Mechanism Using <sup>1</sup>H-NMR Studies

To investigate the decrosslinking mechanism, *t*-BAEM-IPDI-*t*-BAEM was refluxed in toluene with either 2 equiv diisobutylamine or bis(2-ethylhexyl)amine. The solvent was then removed and the resultant was analyzed by <sup>1</sup>H-NMR. The presence of *t*-BAEM-IPDI-*t*-BAEM, residual toluene, the added amine in each sample, and any reflux reaction products resulted in a complex

<sup>1</sup>H-NMR spectrum with overlapping peaks from which no individual structures could be determined. However, in both amine samples an isolated triplet at 2.87 ppm appeared after reflux. The <sup>1</sup>H-NMR spectrum of *t*-BAEM-IPDI-*t*-BAEM showed no peak present there. However, *t*-BAEM, one of the starting materials used to form the *t*-BAEM-IPDI-*t*-BAEM, does have a peak at 2.87 ppm that corresponds to the —CH<sub>2</sub>—NH—(C(CH<sub>3</sub>)<sub>3</sub>). The *t*-BAEM-IPDI-*t*-BAEM peak that corresponds to the bound —CH<sub>2</sub>—NH(C(CH<sub>3</sub>)<sub>3</sub>) occurs at 3.53 ppm. The refluxed diisobutylamine sample had, in addition to the free *t*-BAEM peak at 2.87 ppm, a very small peak at 3.53 ppm that corresponded to the bound *t*-BAEM. This suggests that the cleaving reaction did not go to 100%. The bis(2-ethylhexyl)amine sample showed no peak corresponding to bound *t*-BAEM; this indicates that this reaction did proceed until no discernable amount of bound *t*-BAEM could be detected. This lends further proof that bis(2-ethylhexyl)amine is more reactive than diisobutylamine, which is in agreement with experimental data. Free *t*-BAEM, present in the samples, could only have come from the severing of the urea linkages by amine. Therefore, these results suggest that the disassembly mechanism for this network is the amine severing the urea linkages, resulting in free *t*-BAEM and the amine-IPDI-amine byproduct.



## SUMMARY AND CONCLUSIONS

The use of sterically hindered urea linkages incorporated into these crosslinker molecules facilitated disassembly via amine and alcohol severing agents. As the basic strength increases, the decrosslinking temperature decreases. However, although basic strength is the primary factor, a secondary factor, the steric hindrance around the attacking site on the basic cleaving agent, provides a method to fine tune the rework temperature. Therefore, it would be possible to design a material with a range of rework temperatures merely by selecting the appropriate severing agent with the correct basicity and sterics. Thermal degradation data suggest that the network is stable in the absence of decrosslinking agents. Therefore, the network does not disassemble because of inherent thermal instability. Finally,  $^1\text{H-NMR}$  data show that the decrosslinking agent severs the sterically hindered urea linkages.

In experiments where the molar amounts of the decrosslinking agent did not equal the molar quantities of the sterically hindered urea linkages, the networks were more stable than when 2 equiv of decrosslinking agent were used. Two reasons are suggested. First, not enough decrosslinking agent is present to push the equilibrium in favor of complete decrosslinking. Second, some reworkable crosslinkers are left structurally intact. This would result in some decrosslinking as a function of temperature, which is observed, but enough crosslinkers may be left intact to maintain the overall integrity of the matrix.

This type of system suggests a possible prototype for a material that would be reworkable, hence, allowing easy recycling of components as they become defective or worn. The method described is not limited to just these disassembly temperatures but any temperature is possible by careful selection of the cleaving agent. This versatility allows its application in any process where temperature sensitivity is also a factor in the recycling and upper temperature limits exist as to what is considered an acceptable recycling temperature.

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