Thermal Degradation of Polymers

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The following is a summary of the article "Computer-aided Chemistry Techniques Reveal Thermal Degradation mechanisms of Polymers" published in Scientific Computing & Automation[1].

Abstract

An approach to predicting and understanding thermal degradation mechanisms of polymers is described. MOPAC PM3[2] calculations on Nylon 66 using the CAChe WorkSystem[3] software corroborate experimental observations[4,5,6,8] and provide new insights into the thermal degradation mechanisms of Nylon. Formation of cyclopentanone by thermal degradation, previously reported in the literature[8] as unexplained, is hereby rationalized.

Introduction

Experimental tests are both time-consuming and expensive because they require that a new polymer actually be synthesized and processed. The ability to predict thermal degradation mechanisms and thermodynamics by computer-aided chemistry can save significant time and money, as little or no experimental work may be required.

Further, the computer-aided chemistry approach often provides new insights into the mechanism of thermal decomposition and formation of breakdown products that are unavailable by experimental techniques. This ability to explore the relationship between a molecule's structure and its chemical and physical properties allows for a more systematic approach to the design of new polymers and processes.

Approach

For expediency, the smallest representative section of each polymer or polymer fragment to be investigated was sketched in the **CAChe Workspace** and entered into a **CAChe ProjectLeader** spreadsheet. The polymer and radical fragments typically varied between one and two repeat units for most of the calculations performed here. Various properties such as heats of formation and Gibbs free energies at different temperatures were automatically calculated in the spreadsheet using the default procedures based on MOPAC PM3.
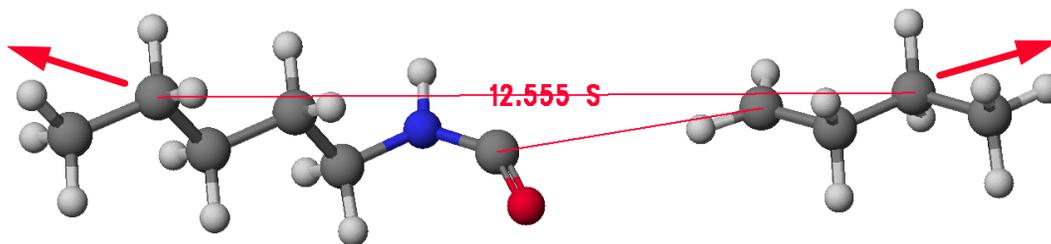

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Figure 1. Stretch to breaking point

*The basis for this calculation is the **map reaction** property (MOPAC PM3 UHF optimized reaction coordinate). The CAChe WorkSystem automates the set up, calculation and graphical interpretation of the results for the user.*

Stretch to breaking point

In the absence of specific reactions, such as a retro Diels-Alder, condensation or hydrolysis reactions, etc., the initial step in any thermal decomposition is likely to be bond homolysis. It is assumed that the weakest bond will break first on heating, and that the weakest bond will also break first on stretching the chain. Thus, to identify the weakest bond, equivalent atoms at each end of the repeat unit were pulled until a bond snapped. This was modeled by placing a **Search Label** between the atoms at each end of the polymer repeat unit. Using the **Map reaction** property, the atoms were pulled apart in increments of 0.05 Angstroms and re-optimized at each step until the chain broke, as illustrated in **Figure 1**. The **multiplicity** setting for the MOPAC PM3 procedure for this calculation was changed to **UHF** to allow for unpaired electrons (radicals).
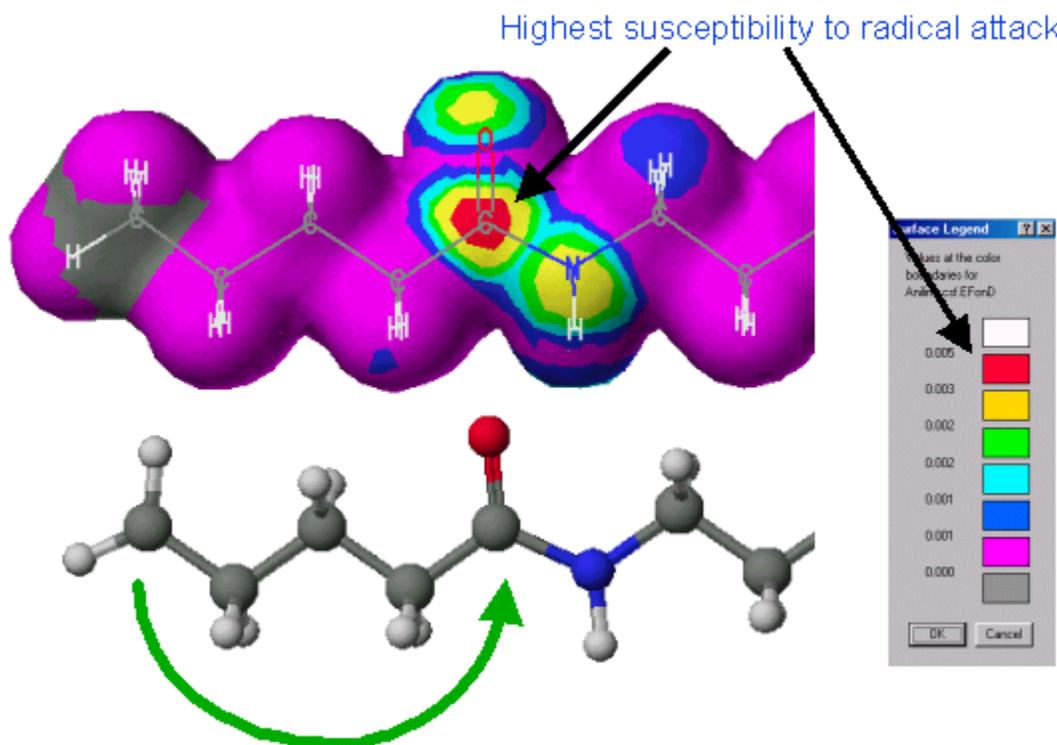
**Figure 2.** Radical attack forms cyclopentanone

*The radical susceptibility surface shown here is derived from Fukui's Frontier Density theory[6] and is created by calculating the **radical susceptibility** property in CAChe.*

Degradation products

This first bond that breaks leaves a free methylene radical and a free carbonyl radical. **Figure 2** was generated by calculating the **radical susceptibility** property of the Nylon chain and shows that the carbonyl carbon is the part of the Nylon 66 chain that is most susceptible to free radical attack[6] (an arrow points at the highest radical susceptibility, shown in red). If the methylene radical were to fold back and attack this susceptible carbonyl carbon, then cyclopentanone could be formed. Cyclopentanone is, indeed, reported as one of the major thermal breakdown products[4,7,8] of Nylon 66.

Comparing kinetic barriers of each bond dissociation
An alternative and more systematic approach is to stretch each individual bond to its breaking point (rather than the repeat unit as a whole) and plot the heat of formation (enthalpy) as a function of bond extension, as shown in **Figure 3**. In any case, this approach may be necessary to account for homolysis in side chains, which would be unaffected by stretching the repeat unit.
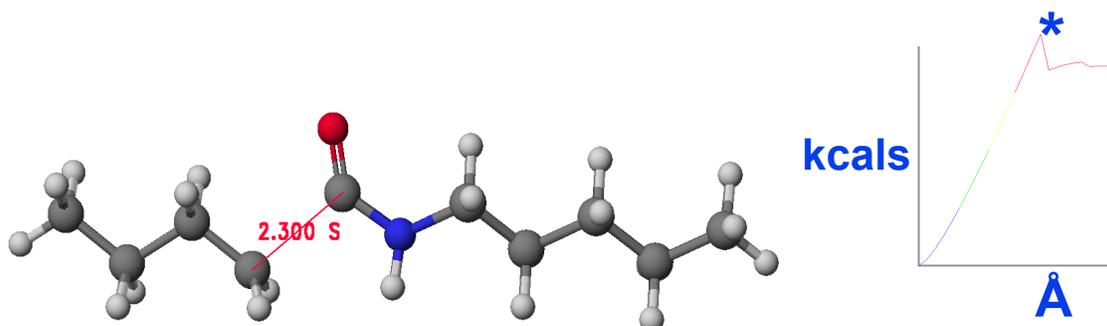
Figure 3. Map reaction results for the CO-CH$_2$ bond homolysis

The approximate transition state (marked with * in **Figure 3**) was then refined for each bond stretch and the heat of formation calculated to derive the relative kinetic stabilities of every bond as listed in **Table 1**. The lowest energy transition state was that of the carbonyl-methylene bond, which is consistent with the results of the "stretch-to-breaking-point" for the whole repeat unit. The heats of formation of the transition states were typically only a few kcals above the heats of formation of the radical products, i.e. the kinetic barriers were only slightly higher than the heats of reaction.

| bond number	transition state	heat of formation (kcal/mole)	all negative vibrations (cm-1)
1	Nylon C-C(CCN) ts	-29.7	-153.3
2	Nylon C-C(CN) ts	-29.6	-171.9
3	Nylon C-C(N) ts	-34.4	-80.3
4	Nylon N-CH2 ts	-24.3	-270.6
5	Nylon N-CO ts	-31.6	-234.5
6	Nylon CO-CH2 ts	-35.5	-85.0
7	Nylon C-C(CO) ts	-26.5	-114.0
8	Nylon C-C(CCO) ts	-27.4	-131.7

Table 1. Backbone bonds homolysis transition state energies

*The approximate transition states from the **map reaction** calculation were refined using the **refine transition state** calculation. **Verify transition state** was then used to generate the vibrational spectrum. A single negative vibration confirms that a true transition state has been found. PM3 calculations are typically accurate to about 8 kcals[2], although, as systematic errors will cancel, the energy differences could be expected to be much more accurate.*

Thermodynamic (heats of formation) calculations revealed that the lowest energy products of hydrogen radical formation were at least 10 kcals higher than the highest of the backbone homolysis products. Hence, the kinetic barriers of hydrogen radical formation would be too high to be the initial bond homolysis step and so were not studied further.

Kinetic versus thermodynamic control
The bond dissociation energies (heat of reaction) for each of the backbone bonds were also calculated (**Table 2**) and are illustrated in **Figure 4**. The three lowest backbone fission enthalpies were calculated to be within one kcal of each other. While the lowest heat of reaction for bond fission (nitrogen-carbonyl bond) did not correspond to the lowest kinetic barrier (carbonyl-methylene bond), the next two bond fission enthalpies did correspond to the two lowest kinetic barriers. Only fission at the carbonyl-methylene bond gives the direct opportunity to form cyclopentanone, the major experimentally observed breakdown product[4,7,8] of Nylon 66. Thus, thermal homolysis of Nylon 66 appears to be controlled by the kinetically predicted bond fission and not the thermodynamically favored products.
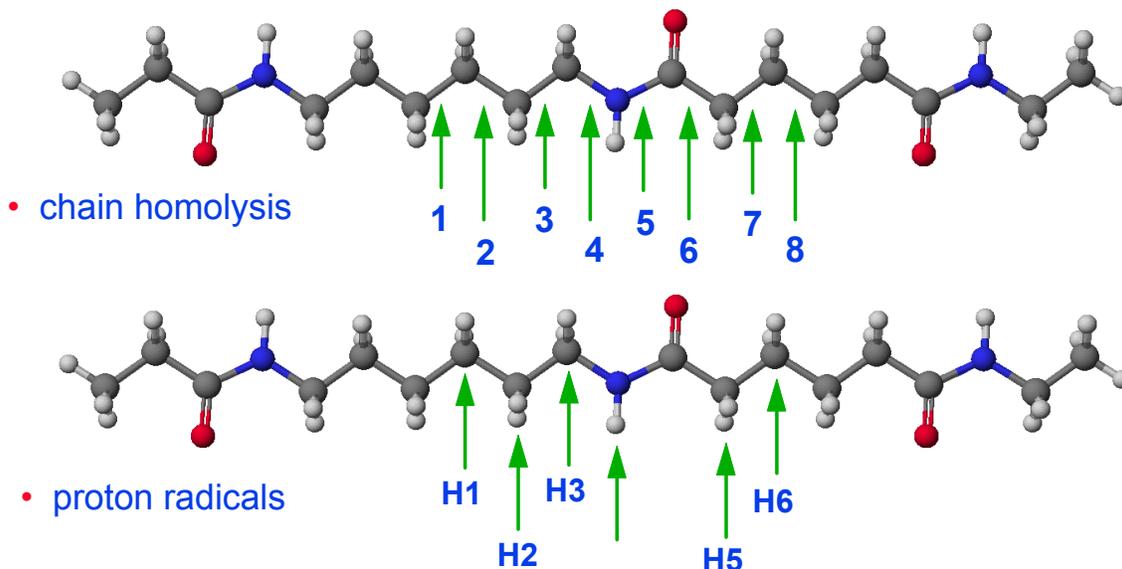
Figure 4. Bonds studied for homolysis calculations

Activation energy
By comparing the ground state and transition state structures, the CACHe WorkSystem also predicted that the Gibbs free energy of activation at 360°C was 41 kcals for the homolysis of the carbonyl-methylene bond. This is in good agreement with the experimentally derived values[5,8] of 34 - 43 kcals. The purer the Nylon sample, the higher is the experimental value observed.

radical A	heat of formation kcal/mol	radical B	heat of formation kcal/mol	total heat of formation	split = /
1a	-30.778	1b	-84.211	-114.989	(C6) C4/C3 (N)
2a	-35.278	2b	-80.262	-115.540	(C6) C3/C2 (N)
3a	-41.865	3b	-79.332	-121.197	(C6) C2/C1 (N)
4a	-46.139	4b	-69.408	-115.547	(C6) C1/N
5a	-44.119	5b	-77.953	-122.071	N/CO
6a	-86.020	6b	-35.518	-121.538	CO/C1 (C4)
7a	-83.660	7b	-30.042	-113.702	(CO) C1/C2 (C4)
8a	-90.420	8b	-24.147	-114.566	(CO) C2/C3 (C4)
Nylon full rad -I	-155.729	H.	52.102	-103.627	CH2 CH. NH / H.

Table 2. Heats of formation of fragments from bond homolysis

Conclusion

A possible mechanism for the production of cyclopentanone from the thermal degradation of Nylon 66 has been uncovered. Computer-aided chemistry can be used to predict and gain insight into the thermal degradation mechanisms of polymers in a fraction of the time it would take to perform the necessary experiments. Such insight facilitates the systematic design of new polymers with more desirable properties.

References:

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