Supporting Information

Revisiting Acetoacetyl Chemistry to Build Malleable Cross-linked Polymer Networks via Transamidation

Zhiyong Liu, Chunyang Yu, Changxu Zhang, Zixing Shi * and Jie Yin

School of Chemistry and Chemical Engineering, State Key Laboratory for Metal Matrix Composite Materials, and Shanghai Key Lab of Electrical Insulation & Thermal Ageing Shanghai Jiao Tong University, Shanghai 200240, P. R. China
Materials

Propyl acetoacetate, butyl acetoacetate, tolyl isocyanate and ethylphenyl isocyanate were purchased from Adamas and used as received. Polybutadiene (PB, Mw=9.4×10^3, PDI=1.15), 2-mercaptoethanol were purchased from Sigma-Aldrich. Methylene-diphenyl 4,4'-diisocyanate (MDI) was kindly provided by BASF. Acetyl ketene was provided by Sinopharm Chemical Reagent Co., Ltd. All other reagents were commercial chemicals and used without further purification.

Characterization and measurements

Attenuated Total Reflection Fourier transformed Infrared Spectroscopy (ATR-FTIR) spectra were recorded on a Perkin-Elmer Spectrum100 FTIR spectrometer (U.K.).

Nuclear magnetic resonance spectrometer (1H-NMR) were recorded using an AVANCE III HD 500 spectrometer (Bruker BioSpin Corp.), TMS was used as an internal standard.

The mechanical properties of prepared films were determined with an Instron 4465 electronic universal testing machine (Instron Corporation, MA, USA) at a crosshead speed of 10 mm min⁻¹. Dumbbell-shaped specimens were cut according to GB/T528 (overall length: 50mm; inner width: 4mm). At least five specimens per experimental point were tested in all mechanical measurements to obtain reliable values.

Differential scanning calorimetry (DSC) analyses were performed on Q2000 (TA Instruments, USA) under nitrogen atmosphere at a heating rate 20 °C min⁻¹.

Thermogravimetric Analyzer (TGA) tests were conducted via Q5000IR. The heating rate was 20
°C min⁻¹ from room temperature to 700 °C.

Dynamic mechanical analysis (DMA) was performed on DMA Q800 (TA Instruments, USA). PBAM-10% film was cut into rectangular strips. The temperature dependence of the storage modulus (G’), loss modulus (G”) and loss factor (tan δ) were recorded from -80 °C to 180°C. The frequency used is 1.0 Hz at a heating rate of 5 °C min⁻¹.

Stress relaxation tests were also conducted on a DMA Q800 (TA Instruments, USA) at different temperatures. The samples were allowed to equilibrate for 5 min at a specified temperature. Then 1% strain was applied and maintained, the stress was recorded.

Liquid chromatography & mass spectrometer (LC-MS): The LC-MS system included a ternary pump, auto sampler, and thermostatic column compartment, diode array detector(Surveyor, Thermo Fisher Scientific, San Jose, CA, USA), and a linear ion trap mass spectrometer(LTQ XL, Thermo Fisher Scientific) equipped with an electrospray ionization (ESI) source.
Propyl 3-oxo-2-(p-tolylcarbamoyl)butanoate (AFA 1) as an example: propyl acetoacetate (0.01 mol) and tolyl isocyanate (0.01 mol) were firstly dissolved in ether (2 ml) in a round bottom flask, and then TEA (0.1 ml) was added. The resulting mixture was stirred at room temperature for 24h. The precipitate was filtered and redissolved in a large amount of ether. The clarified solution was washed with hydrochloric acid (0.1 M) and water three times. Then dried by anhydrous sodium sulfate and the solvent was removed. The obtained product recrystallized three times in ethanol and dried to obtain propyl 3-oxo-2-(p-tolylcarbamoyl)butanoate (AFA 1). $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 18.31 (s, OH), 11.24 (s, NH), 7.54–7.38 (m, Ar-H), 4.24 (t, -O-CH$_2$-), 2.51 (s, Ar-CH$_3$), 2.35 (s, C=C-CH$_3$), 1.80 (m, -CH$_2$-), 1.05 (t, -CH$_3$). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 192.04, 170.78, 169.32, 134.58, 134.28, 129.51, 121.53, 94.92, 66.68, 26.50, 22.05, 20.92, 10.78. LC-MS Calcd for C$_{15}$H$_{19}$NO$_4$ [M+H]$^+$ :277.13, Found : 278.14.
Butyl (Z)-3-hydroxy-2-(p-tolylcarbamoyl)but-2-enoate (AFA 2), \( ^1H \) NMR (500 MHz, Chloroform-d) \( \delta \) 18.31 (s, OH), 11.24 (s, NH), 7.49–7.39 (m, Ar-H), 4.28 (t, -O-CH\(_2\)-), 2.51 (s, Ar-CH\(_3\)), 2.35 (s, C=C-CH\(_3\)), 1.82–1.69 (m, -CH\(_2\)-), 1.55–1.42 (m, -CH\(_2\)-), 1.01 (t, -CH\(_3\)). \( ^{13}C \) NMR (126 MHz, Chloroform-d) \( \delta \) 192.03, 170.78, 169.32, 134.58, 134.27, 129.51, 121.53, 94.93, 64.85, 30.72, 26.49, 20.92, 19.43, 13.73. \textbf{LC-MS} Calcd for C\(_{16}\)H\(_{21}\)NO\(_4\)[M+H]\(^+\) : 291.15, Found : 292.15.

Propyl (Z)-2-((4-ethylphenyl)carbamoyl)-3-hydroxybut-2-enoate (AFA 3), \( ^1H \) NMR (500 MHz, Chloroform-d) \( \delta \) 18.32 (s, OH), 11.25 (s, NH), 7.51–7.42 (m, Ar-H), 4.24 (t, -O-CH\(_2\)-), 2.65 (s, Ar-CH\(_2\)-), 2.52 (s, C=C-CH\(_3\)), 1.80 (m, -CH\(_2\)-), 1.26 (t, Ar-C-CH\(_3\)), 1.05 (t, -CH\(_3\)). \( ^{13}C \) NMR (126 MHz, Chloroform-d) \( \delta \) 192.05, 170.79, 169.32, 141.02, 134.43, 128.33, 121.64, 94.92, 66.67, 28.35, 26.49, 22.04, 15.61, 10.77. \textbf{LC-MS} Calcd for C\(_{16}\)H\(_{21}\)NO\(_4\)[M+H]\(^+\) : 291.15, Found : 292.14.

Butyl (Z)-2-((4-ethylphenyl)carbamoyl)-3-hydroxybut-2-enoate (AFA 4), \( ^1H \) NMR (500 MHz, Chloroform-d) \( \delta \) 18.35 (s, OH), 11.27 (s, NH), 7.53–7.41 (m, Ar-H), 4.28 (t, -O-CH\(_2\)-), 2.66 (s, Ar-CH\(_2\)-), 2.51 (s, C=C-CH\(_3\)), 1.75 (m, -O-C-CH\(_2\)-), 1.53–1.41 (t, -C-CH\(_2\)-C), 1.25 (t, Ar-C-CH\(_3\)), 1.01 (t, -CH\(_3\)). \( ^{13}C \) NMR (126 MHz, Chloroform-d) \( \delta \) 192.04, 170.79, 169.31, 140.99, 134.47, 128.32, 121.60, 94.92, 64.85, 30.73, 28.36, 26.49, 19.44, 15.62, 13.73. \textbf{LC-MS} Calcd for C\(_{17}\)H\(_{23}\)NO\(_4\)[M+H]\(^+\) : 305.16, Found : 306.19.
Figure S2 $^1$HNMR spectrum of AFA 1

Figure S3 $^{13}$CNMR spectrum of AFA 1
Figure S4 $^1$H NMR spectrum of AFA 2

Figure S5 $^{13}$C NMR spectrum of AFA 2
Figure S6 $^1$H NMR spectrum of AFA 3

Figure S7 $^{13}$C NMR spectrum of AFA 3
Figure S8 $^1$HNMR spectrum of AFA 4

Figure S9 $^{13}$CNMR spectrum of AFA 4
X-ray crystallographic characterization of model AFAs

From the results of NMR, there are no differences on amide bond of AFAs and traditional amides. So the stereo-chemical configuration of AFAs is further characterized by X-ray crystallographic since the stereo-chemical configuration is also a main factor for affecting the stabilities of amide bonds. For example, lactams (one kind of amide) are highly reactive because of the distortion from planarity with twisted structure. **Table S1** collected the data from the characterization. **Table S2** summarizes Winkler−Dunitz distortion parameters ($\tau$, $\chi_\text{N}$), the additive distortion parameter $\Sigma(\tau + \chi_\text{N})$, and selected bond lengths of the model AFAs.$^1$  $^2$ Geometric parameters of the corresponding parent benzamide was also included in the table.$^3$ Unexpectedly, it is found that there are no significant differences between model AFAs and benzamide and the amide moieties in 2, 3 and 4 have a typical planar structure. Although AFA 1 has a small deviation from planarity, it cannot be the main factor of the reactivity because different molecules were involved in the trans-reaction. Therefore, the reversibility of the model AFAs does not arise from the dominant “ketonic” character found in strained lactams.$^4$, $^5$
Table S1 Crystal Data and Structure Refinement Summaries for model AFAs

|             | 1                                      | 2                                      |
|-------------|----------------------------------------|----------------------------------------|
| Empirical formula | C_{15}H_{19}N_{4}O_{4}                      | C_{16}H_{21}N_{4}O_{4}                      |
| Fw           | 277.31                                 | 291.34                                 |
| T (K)        | 173                                    | 173                                    |
| λ (Å)        | 1.54178                                | 1.54178                                |
| Crystal system | Triclinic                             | Orthorhombic                           |
| Space group  | P-1                                   | Pbca                                   |
| Hall group   | -P 1                                  | -P 2ac 2ab                             |
| a (Å)        | 7.215(16)                              | 23.9758(4)                             |
| b (Å)        | 7.939(6)                               | 14.0529(3)                             |
| c (Å)        | 12.741(10)                             | 35.8983(6)                             |
| α (deg)      | 83.90(2)                               | 90                                     |
| β (deg)      | 81.18(10)                              | 90                                     |
| γ (deg)      | 79.25(5)                               | 90                                     |
| V (Å³)       | 706.2(18)                              | 12095.2(4)                             |
| Z            | 2                                      | 32                                     |
| d_{calc}(mg/m³) | 1.304                                | 1.280                                  |
| Abs coeff (mm⁻¹) | 0.779                               | 0.752                                  |
| Abs corr     | None                                   | None                                   |
| F(000)       | 296                                    | 4992                                   |
| Crystal size (mm) | 0.05 x 0.04 x 0.03                   | 0.05 x 0.04 x 0.03                     |
| Theta range for data collection | 3.522 to 65.727                        | 2.462 to 66.812                        |
| Limiting indices | -8<=h<=8,                            | -28<=h<=-28,                           |
|               | -9<=k<=9,                             | -15<=k<=16,                            |
|               | -14<=l<=14                           | -42<=l<=42                             |
| Reflections collected/ unique | 7480 / 2343 [R(int) = 0.0803]       | 111904 / 10707 [R(int) = 0.0923]        |
| Bond precision (Å) | 0.0065                              | 0.0041                                 |
| Nref         | 2447                                   | 10741                                  |
| T min,T max | 0.963,0.977                            | 0.965,0.978                            |
| Data completeness | 0.957                               | 0.997                                  |
| Theta(max)   | 65.727                                 | 66.812                                 |
| R(reflections) | 0.0760 (1436)                        | 0.0610 (7055)                          |
| wR2(reflections) | 0.2523 (2343)                    | 0.1653 (10707)                         |
| Refinement method | Full-matrix least-squares on F²       | Full-matrix least-squares on F²        |
| Data / restraints / parameters | 2343 / 0 / 189                     | 10707 / 3 / 800                        |
| GOF (F²)     | 1.056                                  | 1.022                                  |
| Final R indices [I>2sigma(I)] | R1 = 0.0760, wR2 = 0.2101         | R1 = 0.0610, wR2 = 0.1418             |
| R indices (all data) | R1 = 0.1196, wR2 = 0.2523       | R1 = 0.1031, wR2 = 0.1653             |
| Extinction coeff | n/a                                 | n/a                                    |
| Largest diff. peak and hole | 0.266 and -0.272 e.A⁻³          | 1.078 and -0.360 e.A⁻³                 |
|                | 3                        | 4                        |
|----------------|--------------------------|--------------------------|
| AFA            |                          |                          |
| Empirical formula | C_{16} H_{21} N O_{4} | C_{17} H_{23} N O_{4} |
| Fw             | 291.34                   | 305.36                   |
| T (K)          | 173                      | 173                      |
| \( \lambda \) (Å) | 1.54178                 | 1.54178                  |
| Crystal system | Monoclinic               | Monoclinic               |
| Space group    | P2(1)/n                  | P2(1)/c                  |
| Hall group     | -P 2yn                   | -P 2yc                   |
| a (Å)          | 7.2185(4)                | 10.8708(3)               |
| b (Å)          | 23.5903(9)               | 18.3484(4)               |
| c (Å)          | 18.2552(8)               | 16.9536(4)               |
| \( \alpha \) (deg) | 90                      | 90                       |
| \( \beta \) (deg) | 93.937(3)              | 108.410(1)               |
| \( \gamma \) (deg) | 90                      | 90                       |
| V (Å³)         | 3101.3(2)                | 3208.53(14)              |
| Z              | 8                        | 8                        |
| \( d_{calc} \) (mg/m³) | 1.248                   | 1.264                    |
| Abs coeff (mm⁻¹) | 0.733                   | 0.731                    |
| Abs corr       | Semi-empirical from      | None                     |
|                | equivalents              |                          |
| F(000)         | 1248                     | 1304                     |
| Crystal size (mm) | 0.05 x 0.04 x 0.03        | 0.05 x 0.04 x 0.03       |
| Theta range for data collection | 3.065 to 66.801         | 4.820 to 66.588          |
| Limiting indices | -8<=h<=8,          | -12<=h<=12,              |
|                | -28<=k<=27,             | -21<=k<=21,              |
|                | -21<=l<=21              | -20<=l<=20               |
| Reflections collected/ unique | 34813 / 5432 [R(int) = 0.1709] | 29680 / 5648 [R(int) = 0.1851] |
| Bond precision (Å) | 0.0078                  | 0.0023                   |
| Nref           | 5506                     | 5664                     |
| T min,T max    | 0.965,0.978              | 0.966,0.978              |
| Data completeness | 0.987                   | 0.997                    |
| Theta(max)     | 66.801                   | 66.588                   |
| R(reflections) | 0.1027 (2091)            | 0.0663 (5000)            |
| wR2(reflections) | 0.3040 (5432)            | 0.1904 (5648)            |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data / restraints / parameters | 5432 / 253 / 387       | 5648 / 0 / 405           |
| GOF (F²)       | 1.180                    | 1.041                    |
| Final R indices [I>2sigma(I)] | R1 = 0.1027, wR2 = 0.2445 | R1 = 0.0663, wR2 = 0.1820 |
| R indices (all data) | R1 = 0.2076, wR2 = 0.3040 | R1 = 0.0711, wR2 = 0.1904 |
| Extinction coeff | n/a                     | n/a                      |
| Largest diff. peak and hole | 0.660 and -0.276 e.A⁻³  | 0.478 and -0.397 e.A⁻³   |
Figure S10 ORTEP Structure of AFA 1. Selected bond lengths (Å) and angles (deg):

C8-C9, 1.470(6); C8-O1, 1.262(4); C8-N1, 1.345(5); N1-C5, 1.401(6); N1-H1, 0.90(4);

C9-C8-N1-C5, -176.820(374); O1-C8-N1-H1, 176.989(2823); O1-C8-N1-C5, 3.894(673);

C9-C8-N1-H1, -3.724(2850).

Figure S11 ORTEP Structure of AFA 2. Selected bond lengths (Å) and angles (deg): C8-C9,

1.468(4); C8-O1, 1.265(3); C8-N1, 1.341(3); N1-C5, 1.409(3); N1-H1, 0.94(3);

C9-C8-N1-C5, -179.876(244); O1-C8-N1-H1, -179.885(1909); O1-C8-N1-C5, 3.894(673); C9-C8-N1
Figure S12 ORTEP Structure of AFA 3. Selected bond lengths (Å) and angles (deg):

C9-O4, 1.2555(60); C8-N1, 1.3470(62); N1-C11, 1.4191(66); N1-H1, 0.8804(37); C5-C8-N1-C11, 179.873(466); O4-C8-N1-H1, 179.358(451); O4-C8-N1-C11, -0.651(819); C5-C8-N1-H1, -0.118(696).

Figure S13 ORTEP Structure of AFA 4. Selected bond lengths (Å) and angles (deg):

C9-C6, 1.480(2); C9-O3, 1.257(2); C9-N1, 1.341(2); N1-C10, 1.416(2); N1-H1, 0.8876;
C6-C9-N1-C10, -178.557(155); O3-C9-N1-H3, -179.888(149); O3-C9-N1-C10, 1.143(266);
C6-C9-N1-H1,0.411(233).

Table S2. Summary of structural parameters for X-ray structures of model AFAs and reference benzamide

| Sample | C=O (Å) | N-C(O) (Å) | τ (deg) | χN (deg) | τ+χN (deg) |
|--------|---------|------------|--------|----------|------------|
| AFA 1  | 1.262   | 1.345      | 5.058  | 13.809   | 18.867     |
| AFA 2  | 1.265   | 1.341      | 0.03   | 1.383    | 1.413      |
| AFA 3  | 1.255   | 1.347      | 0.588  | 0.018    | 0.606      |
| AFA 4  | 1.257   | 1.341      | 1.244  | 2.063    | 3.307      |
| Benzamide^b | 1.265 | 1.342 | 0 | 0.1 | 0.1 |

^aCrystallographic data have been deposited with the Cambridge Crystallographic Data Center.

^bAn example of planar amide.
LC-MS results of the reaction between model AFA 1 and AFA 4

AFA 1 (0.277 g, 1 mmol) and AFA 4 (0.305 g, 1 mmol) were added into a flask and dissolved in dimethylformamide. The obtained mixture was bubbled with nitrogen for 30 min and then stirred at different temperatures (60-100°C) under nitrogen atmosphere. Aliquots were withdrawn at different times and diluted in acetonitrile to a proper concentration followed by being analyzed by LC-MS. The concentrations of AFA 2 was tracked and calculated with a standard curve.

Figure S14 The results of LC-MS at different reaction times
Figure S15 The mass spectrum of the retention time at 7.46 min

Figure S16 The mass spectrum of the retention time at 8.32 min
Figure S17 The mass spectrum of the retention time at 8.40 min

Figure S18 The mass spectrum of the retention time at 9.37 min
Figure S19 The concentrations of AFA 2 at different transamidation time. Linear fits are shown for initial rates under condition.

Figure S20 Arrhenius analysis of model AFAs transamidation reaction.

**Exclusion of the “isocyanate deblocking” mechanism**

To demonstrate it is not “isocyanate deblocking” reaction realize the malleable cross-linked structure, we referred to previous reports and conducted experiments.
Acetoacetyl group is a common block agent but it is totally different with other block agents (such as phenols, triazoles, hydroxamic acid esters, oximes). Acetoacetyl blocked isocyanates do not yield urethanes or ureas when reacted with hydroxy-functional or amine-functional coreactants as reported.6-9 Here, we conducted an experiment to support our proposed mechanism via “proton switch” process rather than an “isocyanate deblocking” reaction.

In brief, the AFA 2 and propyl acetoacetate were mixed in DMF under N₂ at 90°C for 8h. The resulted solution was analyzed by HPLC as shown in the Figure S21 below.

Figure S21 The exclusion of the “isocyanate deblocking” mechanism from the “proton switch” mechanism

The analysis results illustrated that there is no other new chemicals was generated. If isocyanate was produced, there would be AFA 1 because of the similar reactivity of propyl acetoacetate and butyl acetoacetate. So the reaction would happen as we described in the manuscript. The reactivity...
of amines is higher than propyl acetoacetate leading to the absence of AFA 1.

The functionalization of PB with acetoacetyl groups (PBAA)

Briefly, PB (5.4 g, 0.1mol repeat units) and 2-mercaptoethanol (0.78 g, 0.01 mol) were firstly dissolved in dichloromethane (DCM) in a flask. After adding a trace amount of I907, the solution was stirred and irradiated by a UV lamp (100W, 365nm) for 2h under an inert atmosphere at room temperature. When the thiol-ene “click” reaction was completed, acetyl ketene (1.0 g, 0.012 mol) was added dropwise and the solution was refluxed for another 4h. The resulting solution was concentrated and poured into a large amount of ethanol. The precipitate was washed three times with ethanol, dried to a constant weight and denoted as PBAA. According to the integral area from $^1$H-NMR (Figure S22), the real modification ratio is 9.8 mol% of repeat units.
The demonstration of the reactivity of PBAA

To demonstrate the reactivity of PBAA with isocyanate, we firstly conducted the reaction between PBAA and tolyl isocyanate. Figure S23 shows $^1$H-NMR spectrum of the product, it can be concluded that the reactivity of acetoacetyl groups was reserved when it was introduced into polymer chain.
The preparation of cross-linked polymer networks (PBAM)

Constructing polymer network with recyclability could demonstrate the dynamic nature of the AFAs. General procedure was as follows: PBAA was firstly dissolved in toluene followed by adding different amounts of MDI. The homogeneous solution was cast onto PTFE mold and kept undisturbed at 80 °C for 72 h in an oven to obtain a uniform film denoted as PBAM-x, in which x is the mole percent of the isocyanate groups to PB repeat units. Take PBAM-8 as an example, the amount of isocyanate groups is 8 mol% of PB repeat units. That is, there were residual acetoacetyl groups about 2 mol% of PB repeat units because PBAA contained acetoacetyl groups about 10 mol% of PB repeat units as revealed by $^1$HNMR results. So if x is 10, there were no acetoacetyl groups in PBAM-10.
Determination of gel fraction and swelling ratio

A small piece of film ($m_0$) was submersed in toluene in a sealed bottle and stirred slowly for 3d at 80°C. Then the sample was taken out and wiped by filter paper followed by weighing ($m_1$). Subsequently, the sample was dried in a vacuum oven at 80°C to a constant weight ($m_2$). The swelling ratio (SR) and gel fraction (GF) could be calculated according to equations as follows:

\[ SR = \frac{m_1 - m_2}{m_2} \]
\[ GF = \frac{m_2}{m_0} \]

Where $m_0$ is the weight of the film before immersing in solvent and $m_1$ is the weight when it was taken out. $m_2$ is the weight of sample after drying.
The thermal properties of PBAM-x

Figure S24 TGA curve and its derivative curve of PBAM-10

Figure S25 TGA curve and its derivative curve of PBAM-8
Figure S26 TGA curve and its derivative curve of PBAM-6

Figure S27 DSC curves of PBAM-6, PBAM-8 and PBAM-10
Calculation of activation energies ($E_a$) and topology-freezing transition temperatures ($T_v$)

$E_a$ and $T_v$ were determined using the methodology reported in literature. The relaxation times $\tau^*$ were plotted versus 1000/T. The plots were fit to the Arrhenius law eq 1 and Figure S28:

$$\tau^* (T) = \tau_0^* e^{E_a/RT} \quad (eq\ 1)$$

Eq 1 can be transformed to eq 2

$$\ln \tau^* (T) = \ln \tau_0^* + \frac{E_a}{R} T \quad (eq\ 2)$$

($R$ : universal gas constant; 8.31 J K$^{-1}$ mol$^{-1}$)

Referring to Figure S28, eq (10) for PBAM-10 is transformed into eq (3)

$$\ln \tau (T) = 10.9361 \cdot \frac{1000}{T} - 22.3108 \quad (eq\ 3)$$

$E_a/R= 10.9361$, so the activation energy for PBAM-10 is 91 kJ mol$^{-1}$.

$T_v$ is defined to be the temperature at which the material reaches a viscosity of $10^{12}$ Pa. The relation of the viscosity $\eta$ and the characteristic relaxation time $\tau^*$ is known as the Maxwell relation (eq 4).

$$\eta = G \cdot \tau^* = \frac{E'}{2 (1 + \nu)} \cdot \tau^* \quad (eq\ 4)$$

($G$ : shear modulus, $E'$ : storage modulus, $\nu$ : Poisson's ratio)

Using the poisson’s ratio of PB is 0.5, eq (13) can be transformed to eq (5)

$$\eta = \frac{E'}{3} \cdot \tau^* \quad (eq\ 4)$$

Using these values and eq 2, $T_v$ was calculated to be 35°C.
Recycling procedure of bulk samples

Reprocessing of PBAM-10 was conducted on a press vulcanizer. The PBAM-10 films were firstly cut into pieces, then piled up into a steel mould (d = 40mm) and reprocessed under 10 MPa at 160 °C for 30 min. After cooling down to room temperature, the film was taken out and subjected to a series of tests.
Figure S30 ATR-FTIR spectra of the original samples and the recycled samples

Figure S31 DSC curves of the original samples and recycled samples
Table S3 Summary of the main properties of PBAM-x.

| Sample  | Elastic modulus (MPa) | Strain at break (%) | Stress at break (MPa) | Toughness$^a$ (MJ m$^{-3}$) | GF (%) | SR (%) | Tg$^b$ (°C) |
|---------|-----------------------|---------------------|----------------------|-----------------------------|--------|--------|------------|
| PBAM-10 | 6.0±0.2               | 87±4                | 5.4±0.2              | 2.6±0.1                     | 96±2   | 514±25 | -6         |
| PBAM-8  | 2.3±0.1               | 108±5               | 3.0±0.1              | 1.6±0.1                     | 92±2   | 718±40 | -10        |
| PBAM-6  | 0.9±0.1               | 135±5               | 1.4±0.1              | 0.9±0.1                     | 85±2   | 784±30 | -14        |

$^a$: Toughness was calculated from the area under the stress-strain curves.

$^b$: Tg was determined by DSC using the last cycle of heating curves at the rate of 20 °C min$^{-1}$. We selected the intersection of two tangents as the Tg.

**Computational Details**

To assess the “proton switch” mechanism of the model AFAs, DFT calculations were performed with the Gaussian09 program.$^{10}$ Geometry optimization of reactant structure, transition state structure and product structures were carried out at B3LYP/6-31+G* level without any symmetry restriction.$^{11-13}$ After the geometry optimization was performed, analytical vibration frequencies were calculated at the same level to determine the nature of the located stationary point or the transition state. In addition, the transition state was analyzed by calculating an intrinsic reaction coordinate (IRC).$^{14,15}$

Herein, AFA 1 was selected as a model substrate to predict an Ea value for the generation of ketenes and amines. The DFT-based transition-state (TS) structure of AFA 1 was illustrated in Figure S32. The reactant showed two intramolecular hydrogen bonds (1.472 Å and 1.773 Å) and
transformed into intermediate with an active energy of 77.39 kJ mol$^{-1}$. DFT calculations indicated that intermediate exhibited a N-H dative bond length of 2.076 Å and the O-H bond length was 0.979 Å. Moreover, a real transition state TS was obtained from intermediate with an active energy of 11.55 kJ mol$^{-1}$. It was worth noting that the length of N-H dative bond was shortened to 1.235 Å while the O-H bond length became longer (1.252 Å). Then the amines and ketenes were formed via intramolecular hydrogen transfer from O to N. The computed activation energy was close to the experimentally measured activation parameters including the activation energy from stress relaxation (91 kJ mol$^{-1}$) and the kinetic study of model AFAs (108 kJ mol$^{-1}$).

Figure S32. The DFT calculations for the proposed mechanism
Reactant (atomic coordinates):

| Center Number | Atomic Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|---------------|-------------|------------------------|
| 1             | 6             | 0             | 2.735152    | 0.1558417 0.572416    |
| 2             | 6             | 0             | 3.054927    | -2.163010 0.346005    |
| 3             | 6             | 0             | 3.257672    | -1.320439 0.752310    |
| 4             | 6             | 0             | 3.150266    | 0.070756 0.658397     |
| 5             | 6             | 0             | 2.829174    | 0.656898 -0.574387    |
| 6             | 6             | 0             | 2.623319    | -0.177160 -1.688928   |
| 7             | 1             | 0             | 2.570985    | -2.177465 -2.452402   |
| 8             | 1             | 0             | 3.508567    | -1.755301 1.717725    |
| 9             | 1             | 0             | 3.313603    | 0.692979 1.526524     |
| 10            | 1             | 0             | 2.375039    | 0.264969 2.651640     |
| 11            | 6             | 0             | 3.166394    | -3.665693 -0.224926   |
| 12            | 1             | 0             | 2.200695    | -4.155872 -0.406638   |
| 13            | 1             | 0             | 3.878278    | -4.076229 -0.952331   |
| 14            | 1             | 0             | 3.503841    | -3.960258 0.774460    |
| 15            | 7             | 0             | 2.692555    | 2.044608 -0.800904    |
| 16            | 6             | 0             | 2.826753    | 3.076503 0.062978     |
| 17            | 8             | 0             | 3.116054    | 2.878445 1.276113     |
| 18            | 6             | 0             | 2.625513    | 4.467762 -0.444960    |
| 19            | 6             | 0             | 2.771271    | 5.512788 0.480058     |
| 20            | 8             | 0             | 3.072868    | 5.269408 1.738065     |
| 21            | 6             | 0             | 2.622097    | 6.988807 0.229115     |
| 22            | 1             | 0             | 1.622592    | 7.231501 -0.140836    |
| 23            | 1             | 0             | 2.801808    | 7.507550 1.173260     |
| 24            | 1             | 0             | 3.332096    | 7.338652 -0.524798    |
| 25            | 6             | 0             | 2.290119    | 4.691972 -1.859785    |
| 26            | 8             | 0             | 2.133500    | 5.985288 -2.214383    |
| 27            | 6             | 0             | 1.802393    | 6.238669 -3.603533    |
| 28            | 6             | 0             | 1.673198    | 7.743804 -3.783940    |
| 29            | 1             | 0             | 0.869269    | 5.717803 -3.842318    |
| 30            | 1             | 0             | 2.592569    | 5.818710 -4.234631    |
| 31            | 6             | 0             | 1.322209    | 8.109365 -5.231935    |
| 32            | 1             | 0             | 0.900156    | 8.123737 -3.103585    |
| 33            | 1             | 0             | 2.616660    | 8.224226 -3.494286    |
| 34            | 1             | 0             | 1.232279    | 9.194958 -5.347357    |
| 35            | 1             | 0             | 2.093630    | 7.763346 -5.931084    |
| 36            | 1             | 0             | 0.368425    | 7.662174 -5.538443    |
| 37            | 8             | 0             | 2.151293    | 3.799629 -2.700666    |
| 38            | 1             | 0             | 2.456756    | 2.333102 -1.753061    |
Intermediate (atomic coordinates):

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 0.153962 3.876120 -3.063806 |
| 2             | 6             | 0           | -0.203251 5.228813 -2.947900 |
| 3             | 6             | 0           | -0.775061 5.652682 -1.741329 |
| 4             | 6             | 0           | -0.967320 4.764466 -0.680564 |
| 5             | 6             | 0           | -0.607782 3.420467 -0.816041 |
| 6             | 6             | 0           | -0.053368 2.972057 -2.022311 |
| 7             | 1             | 0           | 0.585938 3.514120 -3.994718 |
| 8             | 1             | 0           | -1.066122 6.693750 -1.620599 |
| 9             | 1             | 0           | -1.396289 5.116430 0.254959 |
| 10            | 1             | 0           | 0.203781 1.923966 -2.146839 |
| 11            | 6             | 0           | 0.025284 6.190241 -4.091906 |
| 12            | 1             | 0           | 1.096575 6.332963 -4.284603 |
| 13            | 1             | 0           | -0.423153 5.818768 -5.021559 |
| 14            | 1             | 0           | -0.407747 7.173502 -3.880551 |
| 15            | 7             | 0           | -0.858076 2.524069 0.280112 |
| 16            | 6             | 0           | -0.133063 1.358421 0.554119 |
| 17            | 8             | 0           | -0.697059 0.375372 1.010948 |
| 18            | 6             | 0           | 1.362867 1.431292 0.417434 |
| 19            | 6             | 0           | 2.068532 2.417409 1.045040 |
| 20            | 8             | 0           | 1.463384 3.424287 1.719036 |
| 21            | 6             | 0           | 3.556629 2.580759 1.118958 |
| 22            | 1             | 0           | 4.081427 1.943529 0.411563 |
| 23            | 1             | 0           | 3.803304 3.632604 0.938396 |
| 24            | 1             | 0           | 3.901509 2.330729 2.130381 |
| 25            | 6             | 0           | 1.935452 0.311848 -0.365556 |
| 26            | 8             | 0           | 3.142209 -0.123684 0.061343 |
| 27            | 6             | 0           | 3.730060 -1.213613 -0.692705 |
| 28            | 6             | 0           | 5.055981 -1.570553 -0.037780 |
| 29            | 1             | 0           | 3.859567 -0.893708 -1.732757 |
| 30            | 1             | 0           | 3.031161 -2.056390 -0.685892 |
| 31            | 6             | 0           | 5.750208 -2.731026 -0.761939 |
| 32            | 1             | 0           | 5.707549 -0.686882 -0.035231 |
| 33            | 1             | 0           | 4.875646 -1.834874 1.011916 |
| 34            | 1             | 0           | 6.701893 -2.977550 -0.278411 |
| 35            | 1             | 0           | 5.129533 -3.635639 -0.755146 |
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 6             | 0           | -4.616377   | -0.773927   | 1.430110    |
| 2             | 6             | 0           | -4.942475   | -1.360076   | 0.200703    |
| 3             | 6             | 0           | -4.075364   | -1.144012   | -0.882280   |
| 4             | 6             | 0           | -2.924759   | -0.368756   | -0.749118   |
| 5             | 6             | 0           | -2.620783   | 0.203390    | 0.489648    |
| 6             | 6             | 0           | -3.461755   | -0.002003   | 1.582327    |
| 7             | 1             | 0           | -5.267025   | -0.926903   | 2.287774    |
| 8             | 1             | 0           | -4.305236   | -1.585399   | -1.849624   |
| 9             | 1             | 0           | -2.272799   | -0.203855   | -1.601701   |
| 10            | 1             | 0           | -3.213078   | 0.424327    | 2.550640    |
| 11            | 6             | 0           | -6.187448   | -2.201257   | 0.035814    |
| 12            | 1             | 0           | -6.763334   | -2.249443   | 0.965606    |
| 13            | 1             | 0           | -6.843470   | -1.794413   | -0.743914   |
| 14            | 1             | 0           | -5.936695   | -3.229060   | -0.255424   |
| 15            | 7             | 0           | -1.409514   | 1.000672    | 0.628086    |
| 16            | 6             | 0           | -0.149198   | 0.161113    | 0.943259    |
| 17            | 8             | 0           | -0.089797   | -0.338697   | 2.045182    |
| 18            | 6             | 0           | 0.802758    | 0.160652    | -0.134571   |
| 19            | 6             | 0           | 0.655678    | 0.991519    | -1.271081   |
| 20            | 8             | 0           | -0.357618   | 1.779440    | -1.428404   |
| 21            | 6             | 0           | 1.653035    | 1.021010    | -2.402188   |
| 22            | 1             | 0           | 1.148292    | 1.396369    | -3.295909   |
| 23            | 1             | 0           | 2.474763    | 1.701946    | -2.153095   |
| 24            | 1             | 0           | 2.091674    | 0.040862    | -2.601452   |
| 25            | 6             | 0           | 1.964827    | -0.753019   | 0.051615    |
| 26            | 8             | 0           | 3.150087    | -0.155881   | -0.245186   |
| 27            | 6             | 0           | 4.330565    | -0.981993   | -0.105100   |
| 28            | 6             | 0           | 5.541606    | -0.132136   | -0.460810   |
| 29            | 1             | 0           | 4.234731    | -1.852832   | -0.764019   |
| 30            | 1             | 0           | 4.379213    | -1.349135   | 0.925617    |
| 31            | 6             | 0           | 6.849430    | -0.921404   | -0.319961   |
| 32            | 1             | 0           | 5.434689    | 0.236654    | -1.489344   |
| 33            | 1             | 0           | 5.562197    | 0.750285    | 0.191559    |
Product-1 (atomic coordinates):

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | 2.490384 -1.046402 0.170653 |
| 2             | 8             | 0           | 3.378581 -1.777406 0.221104 |
| 3             | 6             | 0           | 1.458761 -0.172534 0.111389 |
| 4             | 6             | 0           | 1.884704 1.256051 0.084733 |

Product-2 (atomic coordinates):

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 6             | 0           | -4.669548 0.051407 -0.91856 |
| 2             | 6             | 0           | -3.229849 0.580583 -0.059027 |
| 3             | 1             | 0           | -2.345442 -1.169326 0.898554 |
|   |   |   |           |           |             |
|---|---|---|----------|----------|-------------|
| 4 | 6 | 0 | -5.556681 | 2.576569 | -1.340862   |
| 5 | 6 | 0 | -5.314488 | 3.153358 | -2.599726   |
| 6 | 6 | 0 | -6.270985 | 4.040055 | -3.116495   |
| 7 | 1 | 0 | -8.153179 | 5.025575 | -2.823207   |
| 8 | 1 | 0 | -6.876565 | 2.415863 | 0.339313    |
| 9 | 1 | 0 | -4.826493 | 1.891018 | -0.914423   |
|10 | 1 | 0 | -6.105342 | 4.506245 | -4.086090   |
|11 | 6 | 0 | -8.936218 | 4.088232 | -0.358768   |
|12 | 1 | 0 | -9.586957 | 4.769289 | -0.918108   |
|13 | 1 | 0 | -9.517972 | 3.184468 | -0.134701   |
|14 | 1 | 0 | -8.703739 | 4.568089 | 0.601191    |
|15 | 7 | 0 | -4.117921 | 2.891207 | -3.289053   |
|16 | 1 | 0 | -3.674600 | 2.015184 | -3.063684   |
|17 | 1 | 0 | -4.164432 | 3.037414 | -4.291719   |

References:

1. Winkler, F. K.; Dunitz, J. D. The non-planar amide group. *J. Mol. Biol.* 1971, 59 (1), 169-182.
2. Szostak, R.; Aube, J.; Szostak, M. An efficient computational model to predict protonation at the amide nitrogen and reactivity along the C-N rotational pathway. *Chem. Commun.* 2015, 51 (29), 6395-6398.
3. Johansson, K. E.; van de Streek, J. Revision of the Crystal Structure of the First Molecular Polymorph in History. *Crystal Growth & Design* 2016, 16 (3), 1366-1370.
4. Wang, Q.; Bennet, A.; Brown, R. S.; Santarsiero, B. Distorted amides as models for activated peptide NC (O) units. 3. Synthesis, hydrolytic profile, and molecular structure of 2, 3, 4, 5-tetrahydro-2-oxo-1, 5-propanobenzazepine. *J. Am. Chem. Soc.* 1991, 113 (15), 5757-5765.
5. Bennet, A. J.; Wang, Q. P.; Slebodka-Tilk, H.; Somayaji, V.; Brown, R. S.; Santarsiero, B. D. Relationship between amidic distortion and ease of hydrolysis in base. If amidic resonance does not exist, then what accounts for the accelerated hydrolysis of distorted amides? *J. Am. Chem. Soc.* 1990, 112 (17), 6383-6385.
6. ZENO W. WICKS, J. New developments in the field of blocked isocyanates. *Prog. Org. Coat.* 1981, 9, 3-28.
7. U. Ro¨ckrath, K. B. t., Th. Frey, U. Poth, G. Wigger. Investigation of the crosslinking mechanism of etch-resistant clearcoats. *Prog. Org. Coat.* 1997, 32, 173–182.
8. Douglas A. Wicks a, Zeno W. Wicks Jr. b. Multistep chemistry in thin films; the challenges of blocked isocyanates. *Prog. Org. Coat.* 2001, 43, 131–140.
9. Wicks, Z. W., Jr.; Wu, K. J. Reactions of Acetoacetic Ester Blocked Cyclohexyl Isocyanate. *The Journal of Organic Chemistry* 1980, 45 (12), 2446-2448.
10. Frisch, M.; Trucks, G.; Schlegel, H.; Seusera, G.; Robb, M.; Cheesman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., 09 Gaussian D. 01 Revision. Gaussian Inc. Wallingford CT:
2013.
11. Becke, A. D. Density-functional thermochemistry. V. Systematic optimization of exchange-correlation functionals. *The Journal of chemical physics* 1997, 107 (20), 8554-8560.
12. Kohn, W.; Becke, A. D.; Parr, R. G. Density functional theory of electronic structure. *The Journal of Physical Chemistry* 1996, 100 (31), 12974-12980.
13. Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* 1980, 58 (8), 1200-1211.
14. Gonzalez, C.; Schlegel, H. B. An improved algorithm for reaction path following. *The Journal of Chemical Physics* 1989, 90 (4), 2154-2161.
15. Gonzalez, C.; Schlegel, H. B. Reaction path following in mass-weighted internal coordinates. *J. Phys. Chem.* 1990, 94 (14), 5523-5527.