Supporting Information

High photosensitive furan acrylate derivatives and its solid state photopolymerization

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1 Experimental Section

1.1 Synthesis of furan acrylic acid

As refer to references,[1] fresh steamed furfural, acetic anhydride, anhydrous K_2CO_3 and PEG400 were added to a 500 mL three-necked flask equipped with a thermometer, mixer and condenser pipe, heat up to 140 ℃ slowly and stirred reflux reaction for 5 h. The final reaction mixture was poured to a 500 mL beaker of water, mixing and stirring to obtain crystal precipitation. The crystal was heated to dissolve and then activated carbon was added to decolorize the filtrate. The filtrate was acidified to a pH of 2 ~ 3 with hydrochloric acid and stood for 8 ~ 12 h, filtration and white furan acrylic acid crystals were obtained. The equation is shown in Figure S1, and the ^{1}H NMR spectrum are shown in Fig.S2.
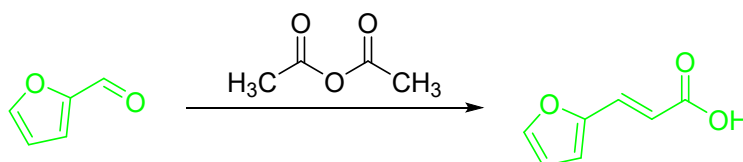
Fig.S1 Synthesis of furan acrylic acid

1.2 study on kinetics of thermal-oxidative decomposition

A TG209F3 thermogravimetric analyzer (Netzsch, Germany) was used to measure the thermo-oxygen decomposition. 5~10 mg polyester samples were weighed and four heating rates were set at 10, 20, 30 and 40 ℃/min, respectively. Oxygen flow rate is 12 mL/min, nitrogen flow rate is 48 mL/min, increasing the temperature from room temperature to 800 ℃.

2 ^{1}H NMR spectrum of furan acrylic acid

Fig. S2 ^{1}H NMR spectrum of furan acrylic acid

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.51 (d, 2H), 6.67 (d, 1H), 6.49 (q, 1H), 6.30 (d, 1H).

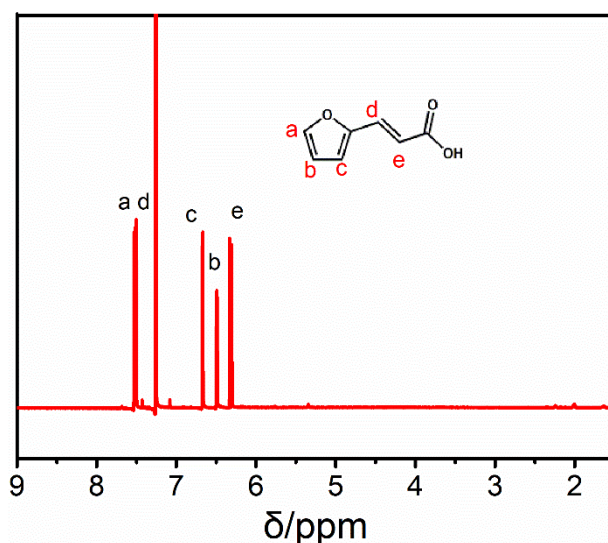# 3 ^{1}H NMR spectrums of diethylene glycol difuran acrylate (DEFA) and Trimethylolpropane trifuran acrylate (TMFA)
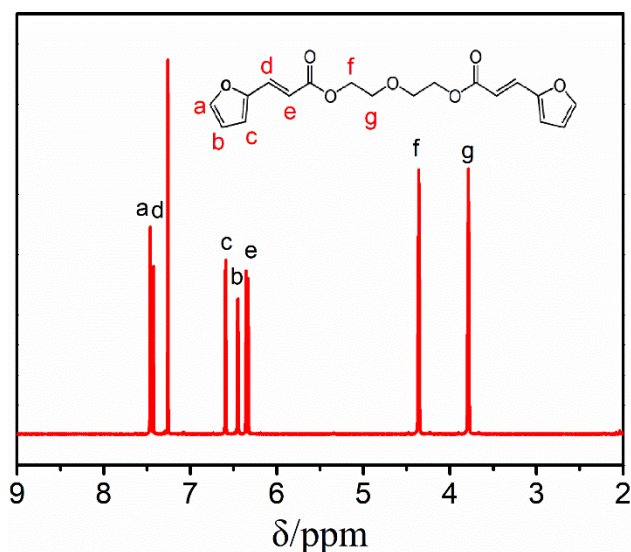
Fig. S3 ^{1}H NMR spectrum of DEFA

^{1}H NMR (500 MHz, CDCl$_3$): δ$_H$ 7.46 (q, 2H), 6.59 (d, 1H), 6.45 (q, 1H), 6.32 (d, 1H), 4.36 (t, 2H), 3.79 (t, 2H).
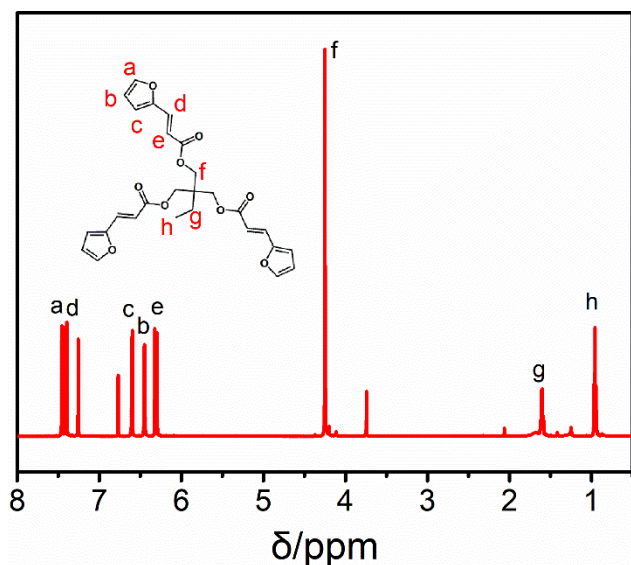
Fig. S4 ^{1}H NMR spectrum of TMFA

^{1}H NMR (500 MHz, CDCl$_3$): δ$_H$ 7.42 (q, 2H), 6.60 (d, 1H), 6.45 (q, 1H), 6.30 (d, 1H), 4.25 (s, 2H), 1.60 (q, 2H), 0.96 (t, 3H).

4 Effect of synthetic conditions on TMFA yield

4.1 Effect of monomer moral ratio on yield of DEFA

Control reaction temperature, time, catalyst dosage unchanged, change the monomer mole ratio. The effect of monomer molar ratio on yield was seen in Tab.S1. With the

increase of the molar ratio of furan acrylic acid to diethylene glycol, the yield first increased and then decreased. When the molar ratio of furan acrylic acid to diethylene glycol was 2.3:1, the yield was the highest.

Tab. S1 Effect of monomer molar ratio on yield of DEFA

No.	furan acrylic acid/mol	diethylene glycol /mol	reaction time/h	Yield/%
1	0.04	0.02	4	25.6
2	0.042	0.02	4	34.5
3	0.044	0.02	4	47.3
4	0.046	0.02	4	53.1
5	0.048	0.02	4	52.8

4.2 Effect of temperature on yield of DEFA

Control monomer mole ratio, reaction time, catalyst dosage unchanged, change reaction temperature. The effect of temperature on yield was seen in Fig.S5. With the increase in reaction temperature, esterification yields first increased and then decreased. When the reaction temperature was 100℃, the yield of DEFA reached the highest about 59.2%.
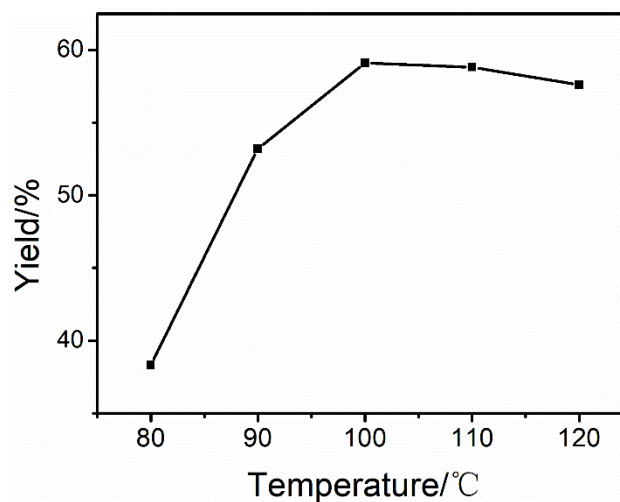

Fig. S5 Effect of temperature on yield of DEFA

4.3 Effect of catalyst dosage on yield of DEFA

Control monomer mole ratio, reaction time, temperature unchanged, change the dosage of p-toluenesulfonic acid. The effect of catalyst dosage on yield was seen in Fig.S6. The yield of DEFA first increased and then decreased with the increase of the catalyst

amount. When the catalyst amount was 3 wt% of the total monomer mass, the yield reached the highest of 68.1%. As the amount of catalyst continues to increase, side reactions are easy to occur and the consumption of reaction raw materials leads to a decline in yield.
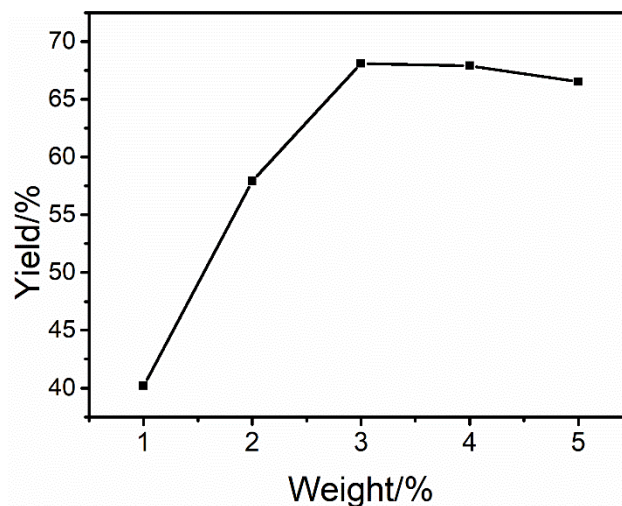

Fig. S6 Effect of catalyst dosage on yield of DEFA

4.4 Effect of reaction time on yield of DEFA

Control monomer mole ratio, reaction temperature, catalyst dosage unchanged, change reaction time. The effect of time on yield was seen in Tab.S2. When the reaction time was 5 h, the yield of DEFA reached 74.7%. To continue to extend the reaction time, there may be side reactions, resulting in a decrease in yield.

Tab. S2 Effect of reaction time on yield of DEFA

No.	reaction time/h	Yield/%
1	2	38.3
2	3	51.2
3	4	68.1
4	5	74.7
5	6	73.9

5. Effect of synthetic conditions on TMFA yield

5.1 Effect of monomer moral ratio on yield of TMFA

Control reaction temperature, time, catalyst dosage unchanged, change the monomer mole ratio. The effect of monomer molar ratio on yield was seen in Tab.S3. With the increase of the molar ratio of TMFA, the yield first increased and then decreased. When

the molar ratio of furan acrylic acid to trimethylolpropane was 3.4:1, the yield was the highest.

<p align="center">Tab. S3 Effect of monomer molar ratio on yield of TMFA</p>

No.	furan acrylic acid/mol	diethylene glycol /mol	reaction time/h	Yield/%
1	0.062	0.02	5	20.7
2	0.064	0.02	5	31.4
3	0.066	0.02	5	40.9
4	0.068	0.02	5	43.5
5	0.070	0.02	5	43.3

5.2 Effect of temperature on yield of TMFA

Control monomer mole ratio, reaction time, catalyst dosage unchanged, change reaction temperature. The effect of temperature on yield was seen in Fig.S7. With the increase in reaction temperature, esterification yields first increased and then decreased. When the reaction temperature was 120℃, the yield of TMFA reached the highest about 48.7%.

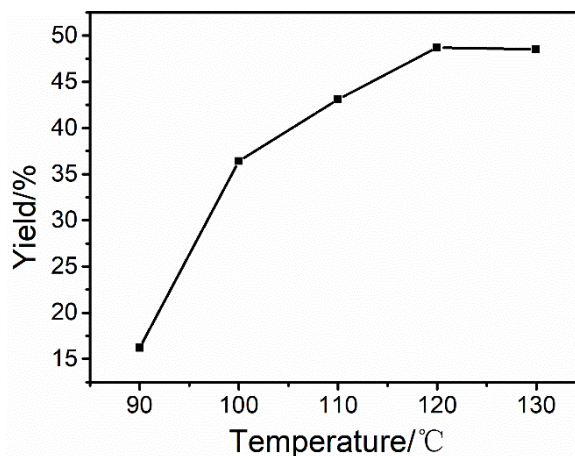<p align="center">Fig. S7 Effect of temperature on yield of TMFA</p>

5.3 Effect of catalyst dosage on yield of TMFA

Control monomer mole ratio, reaction time, temperature unchanged, change the dosage of p-toluenesulfonic acid. The effect of catalyst dosage on yield was seen in Fig.S8. The yield of TMFA first increased and then decreased with the increase of the catalyst amount. When the catalyst amount was 3 wt% of the total monomer mass, the yield reached the highest of 61.1%. As the amount of catalyst continues to increase, side

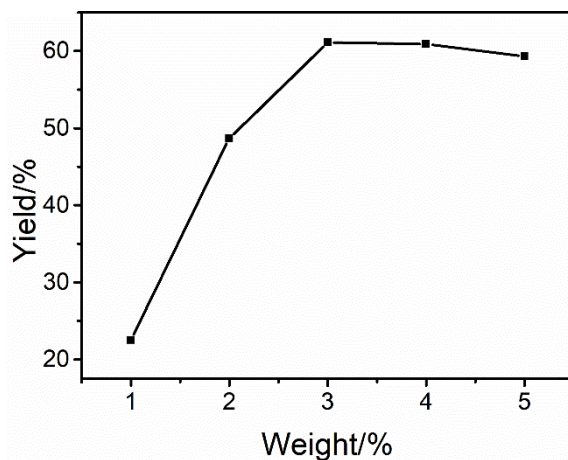reactions are easy to occur, and the consumption of reaction raw materials leads to a decline in yield.

Fig. S8 Effect of catalyst dosage on yield of TMFA

5.4 Effect of reaction time on yield of TMFA

Control monomer mole ratio, reaction temperature, catalyst dosage unchanged, change reaction time. The effect of time on yield was seen in Tab.S4. When the reaction time was 6 h, the yield of TMFA reached 67.5%. To continue to extend the reaction time, there may be side reactions, resulting in a decrease in yield.

Tab. S4 Effect of reaction time on yield of TMFA

No.	reaction time/h	Yield/%
1	2	49.3
2	3	61.1
3	4	67.5
4	5	67.3
5	6	66.9

6. Study on kinetics of thermal-oxidative decomposition

Thermal oxygen stability test of DEFA and TMFA in different air atmosphere obtained the corresponding DTG and TGA curves, respectively, as shown in Figure S9. Tables S5 and S6 show the pyrolysis characteristic parameters of DEFA and TMFA polyester at four different heating rates. It can be shown that the thermal-oxidative decomposition temperature of both DEFA and TMFA increases with increasing the heating rate.

When the heating rate is small, the movement of the kinetic units such as chain links and chain segments of the furan acrylate polyester can keep up with the temperature change under the air atmosphere. However, when the heating rate is larger, the movement of the kinetic units of the furan acrylate polyester cannot keep up with the change of the ambient temperature and shows a certain hysteresis.
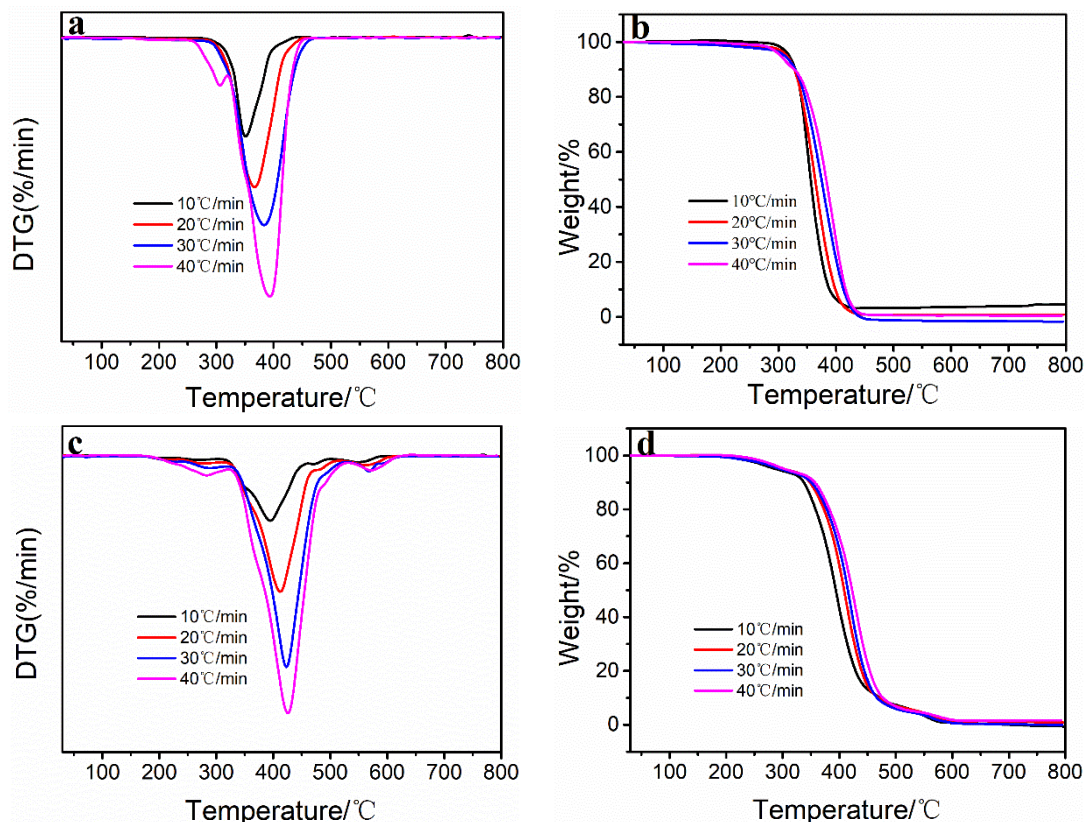

Fig. S9 DTG and TGA curve of DEFA (a,b) and TMFA(c,d) at different heating rates in air atmosphere

Tab.S5 the pyrolysis characteristic parameters of DEFA polyester

heating rate / (°C/min)	initial decomposition temperature /°C	final decomposition temperature/°C	Maximum heat-loss rate temperature/°C
10	281	418	350
20	293	440	366
30	294	449	380
40	292	453	390

Tab.S6 the pyrolysis characteristic parameters of TMFA polyester

heating rate / （°C/min）	initial decomposition temperature /°C	final decomposition temperature/°C	Maximum heat-loss rate temperature/°C
10	233	587	397
20	236	595	411
30	242	600	422
40	246	602	427

The activation energy in the process of thermal oxygen decomposition reflects the difficulty of the material decomposition in the atmosphere. The greater the activation energy, the more difficult the material is to decompose, and the higher the heat required for the decomposition. The activation energy can be obtained by the Kissinger equation method.[2] The formula of the Kissinger method is as follows:

$$\ln\left(\frac{\beta}{T_P^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_P}$$

(1-1)

Where β, E, *A, T_p and R* are the heating rate (K/min), reaction activation energy (kJ/mol), pre-exponential factor (s^{-1}), the temperature at maximum heat-loss rate (K) and gas constant (J/K^{-1}·mol^{-1}), respectively.
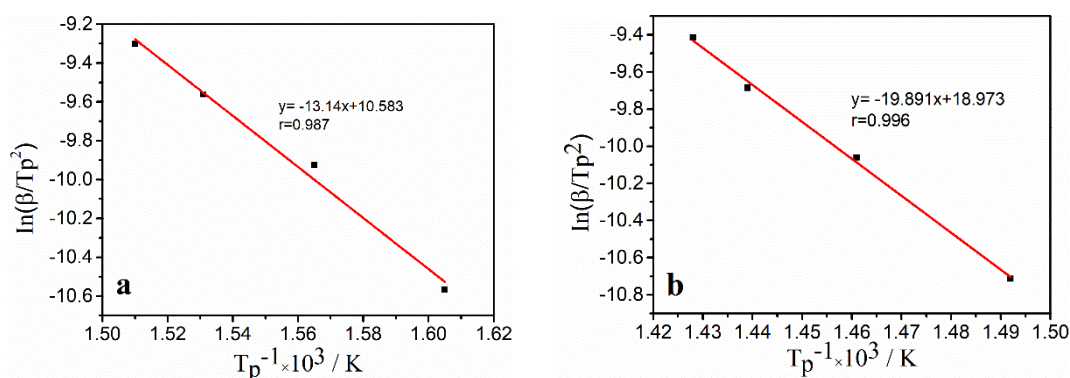

Fig. S10 Linear fitting curve of $\ln(\beta/T_p^2)\sim T_p^{-1}\times10^3$/ K for thermal oxidative decomposition of DEFA (a) and TMFA (b) polyester

From the fitting of $\ln(\beta/T_p^2)\sim T_p^{-1}\times10^3$ in Fig.S10, the reaction activation energy(E) of DEFA linear polyester and TMFA crosslinked polyester is 109.25 kJ/mol and 165.37 kJ/mol, respectively.

7. References

1 M. Hrašna, E. Ürgeová and A. Krutošíková, *Nova Biotechnologica et Chimica*, 2012, **11** (1), 73-85.

2 L. Yang, Y. Liu, C. Ma, Y.Wu, W. Liu, C. Zhang, F. Wang and L. Li, *Fiber. Polym.*, 2016, **17**, 1018-1024.