Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary information

Experimental model design: Exploration and optimization of customized polymerization conditions for the preparation of targeted smart materials by click Diels Alder

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1. **Table S1. Polymerization trials**

Polymerization trials at different water contents and temperatures of monomers DiT-Fur (**1**) or DTT-Fur (**2**) with the bis-maleimide monomer DMDOO (**3**).

Dithiodiethanol (DiT)-based polymers		**Experimental Parameters**		**Dithiothreitol (DTT)-based polymers**	
Sample	**Formulation code**	**Water content (%)**	**Temperature (°C)**	**Formulation code**	**Sample**
A1	**DiT-W_0-T_{20}**	0	20	**DTT-W_0-T_{20}**	**B1**
A2	**DiT-W_0-T_{30}**	0	30	**DTT-W_0-T_{30}**	**B2**
A3	**DiT-W_0-T_{40}**	0	40	**DTT-W_0-T_{40}**	**B3**
A4	**DiT-W_{10}-T_{20}**	10	20	**DTT-W_{10}-T_{20}**	**B4**
A5	**DiT-W_{10}-T_{30}**	10	30	**DTT-W_{10}-T_{30}**	**B5**
A6	**DiT-W_{10}-T_{30}**	10	30	**DTT-W_{10}-T_{30}**	**B6**
A7	**DiT-W_{10}-T_{40}**	10	40	**DTT-W_{10}-T_{40}**	**B7**
A8	**DiT-W_{20}-T_{20}**	20	20	**DTT-W_{20}-T_{20}**	**B8**
A9	**DiT-W_{20}-T_{30}**	20	30	**DTT-W_{20}-T_{30}**	**B9**
A10	**DiT-W_{20}-T_{40}**	20	40	**DTT-W_{20}-T_{40}**	**B10**
[Bis-maleimide monomer] = [Difurfuryl monomer] = 65 mM; polymerization time: 48 h. Solvent: THF with variable water content (in %v/v): 0%, 10% or 20%. Temperature: 20 °C, 30 °C, 40 °C.					

2. Determination of $\bar{D}P$ and $\bar{M}_n$ from ^{1}H NMR

For Type-A polymers and Type-B polymers, the Equations S1a and S2 and S1b and S2 were used, respectively, to determine the number average molecular weight ($\bar{M}_n$) of the synthesized polymers using the integral values of selected ^{1}H NMR signals and the following equations:

$$\bar{D}P = \frac{Hf - \frac{polymer}{4}}{Ha - terminal\ furan} \qquad \text{(Equation S1a)}$$

$$\bar{D}P = \frac{Hb - \frac{polymer}{2}}{Ha - terminal\ furan} \qquad \text{(Equation S1b)}$$

$$\bar{M}_n = [(\bar{D}P * 708) + 400 + 308] \qquad \text{(Equation S2)}$$

where $\bar{D}P$ is the degree of polymerization calculated by ^{1}H NMR. In the case of Type-A polymers, the ratio was calculated between the pondered area of the signal H_f-polymer at δ 4.34 ppm and the area of the Ha-furan peak at δ 7.35 ppm due to the end group found in the polymer chain; in the case of Type-B polymers, the peaks selected were peaks H_b-polymer at δ 5.26 and 5.11 ppm and the peak correlated with the terminal furan ring at δ 7.58 ppm. $\bar{M}_n$ is the number average molecular weight of the polymer calculated by the sum of the mass corresponding to the repeating units (708 Da each) and those of the terminal groups of the polymer chains (400 Da and 308 Da, respectively).

3. Determination of *endo/exo* ratios from ^{1}H NMR

The estimation of the *endo/exo* ratios in the polymeric materials by ^{1}H NMR was straightforward. In the case of **Type-A polymers**, the molar *endo/exo* ratios were calculated according to Equation S3a

$$\frac{endo}{exo} molar\ ratio = \frac{Hb(endo) + Hc(endo)}{Hb\ and\ Hc\ (exo)} \qquad \textit{(Equation S3a)}$$

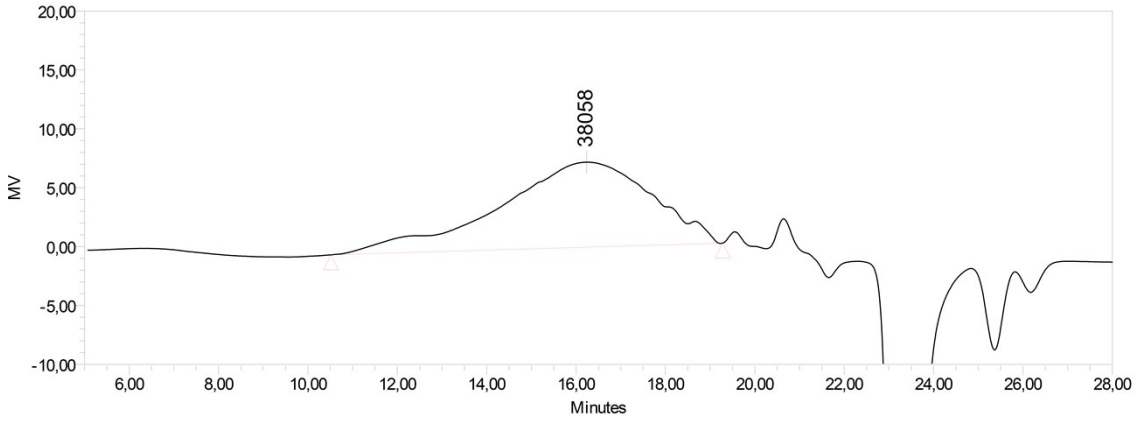
where the integrals of the broad singlets at δ 6.42 and 6.33 ppm corresponding to protons H_b and H_c from *endo* adducts are represented as *Hb(endo)* and *Hc(endo)*, respectively; the integral of the singlet at δ 6.53 ppm, linked to H_b and H_c protons from the *exo* adducts is denoted as *Hb* and *Hc (exo)*.

For **Type-B polymers**, the molar *endo/exo* ratios were calculated according to Equation S3b

$$\frac{endo}{exo} molar\ ratio = \frac{Ha(endo)}{Ha\ (exo)} \qquad \textit{(Equation S3b)}$$

where the integral of the broad singlet at δ 5.25 ppm, linked to protons H_a from *endo* adducts, is represented as *Ha(endo)*; the integral of the broad singlet at δ 5.10 ppm, correlated to H_a protons from the *exo* adducts is denoted as *Ha (exo)*.

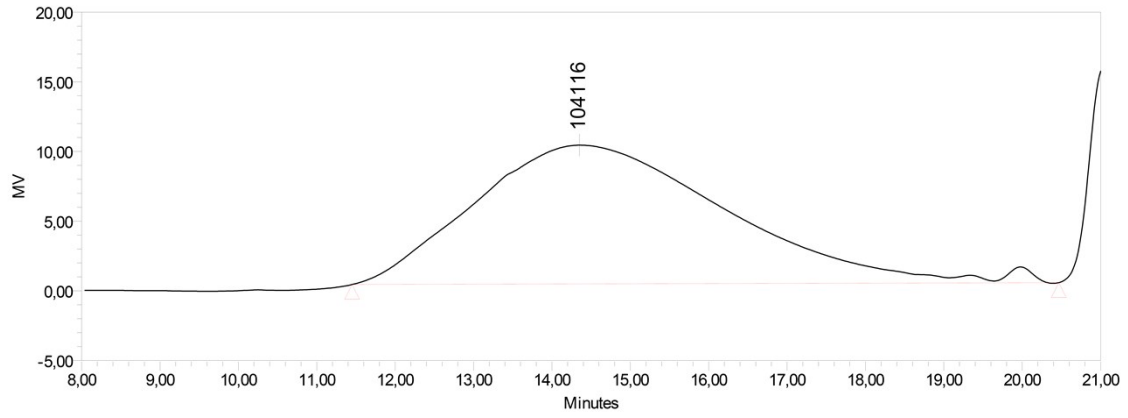
4. GPC chromatograms



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		*42188*	*65271*	*38058*	*102566*	*135988*		*1,547153*		

Figure S1. GPC chromatogram for sample **A3** (**DiT-W_0-T_{40}**).

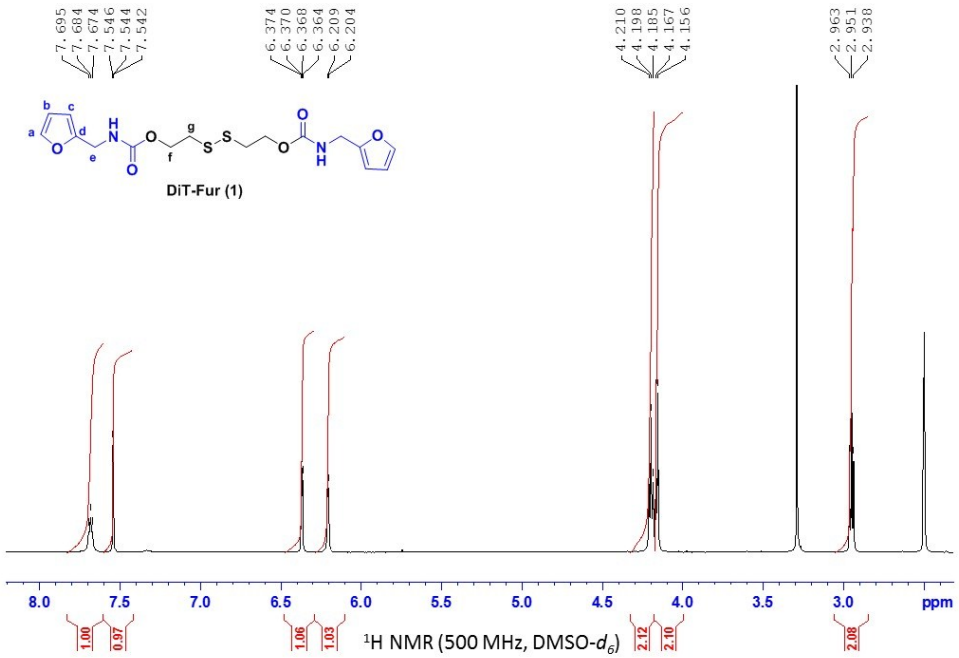


GPC Results

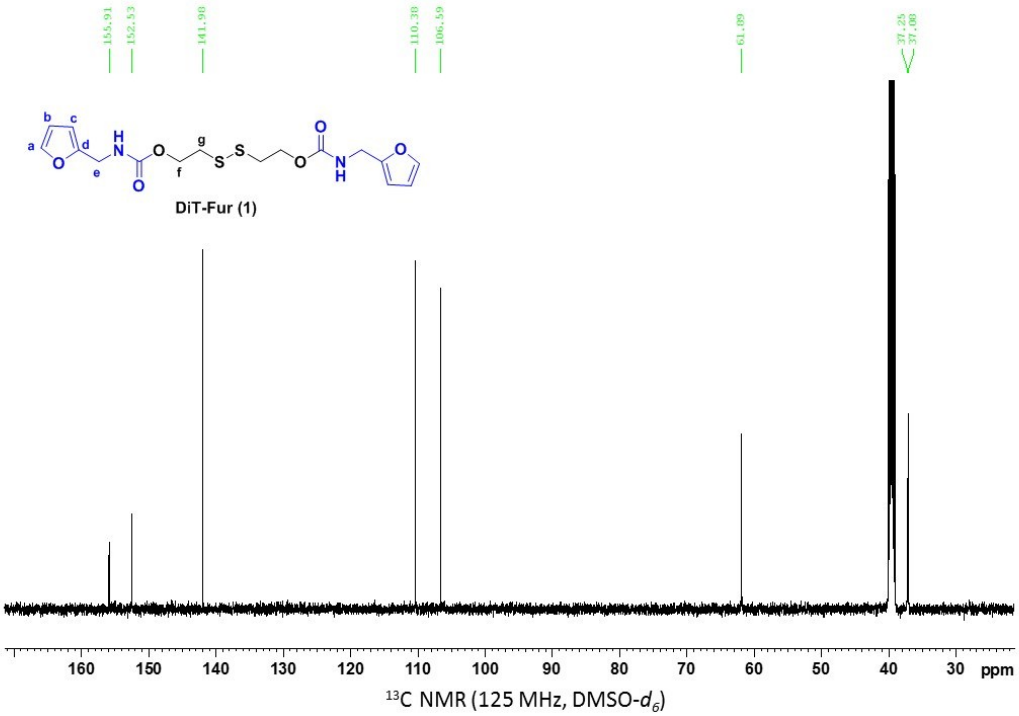
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		*64584*	*95506*	*10411€*	*124571*	*144351*		*1,478788*		

Figure S2. GPC chromatogram for sample **B4** (**DTT-W_{10}-T_{20}**).

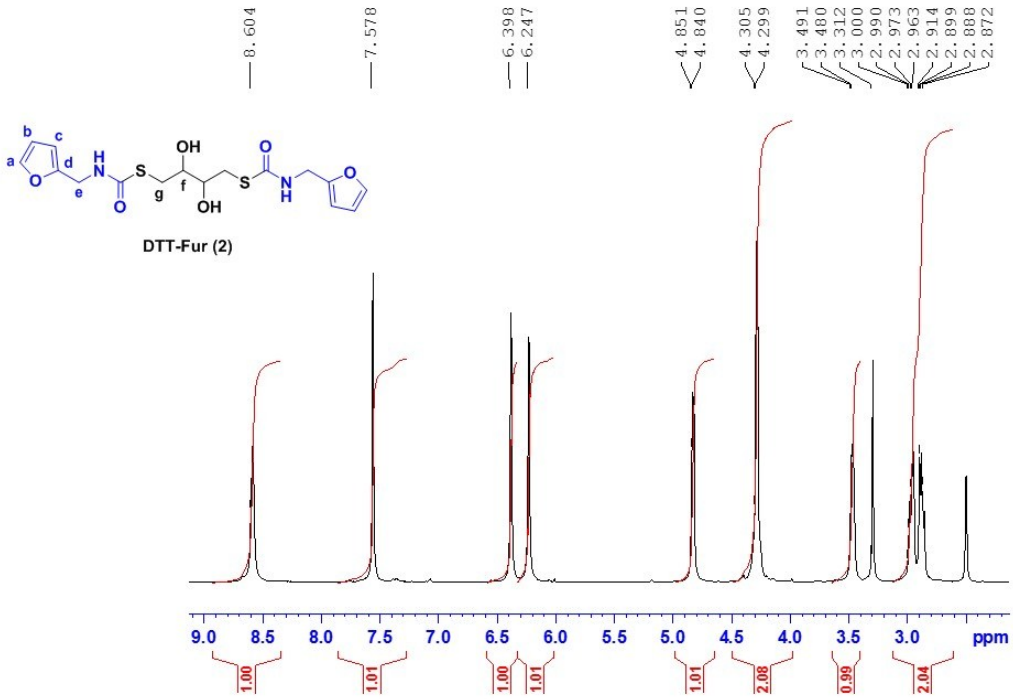
5. ^{1}H NMR and ^{13}C NMR spectra



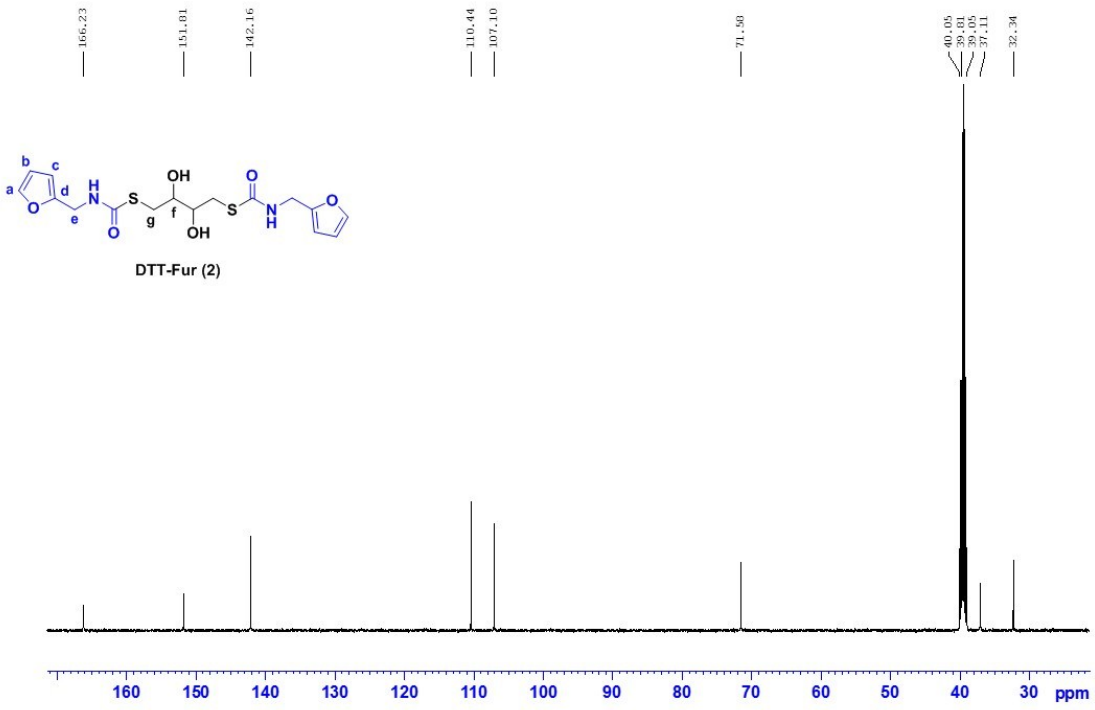
^{1}H NMR (500 MHz, DMSO-d_6)



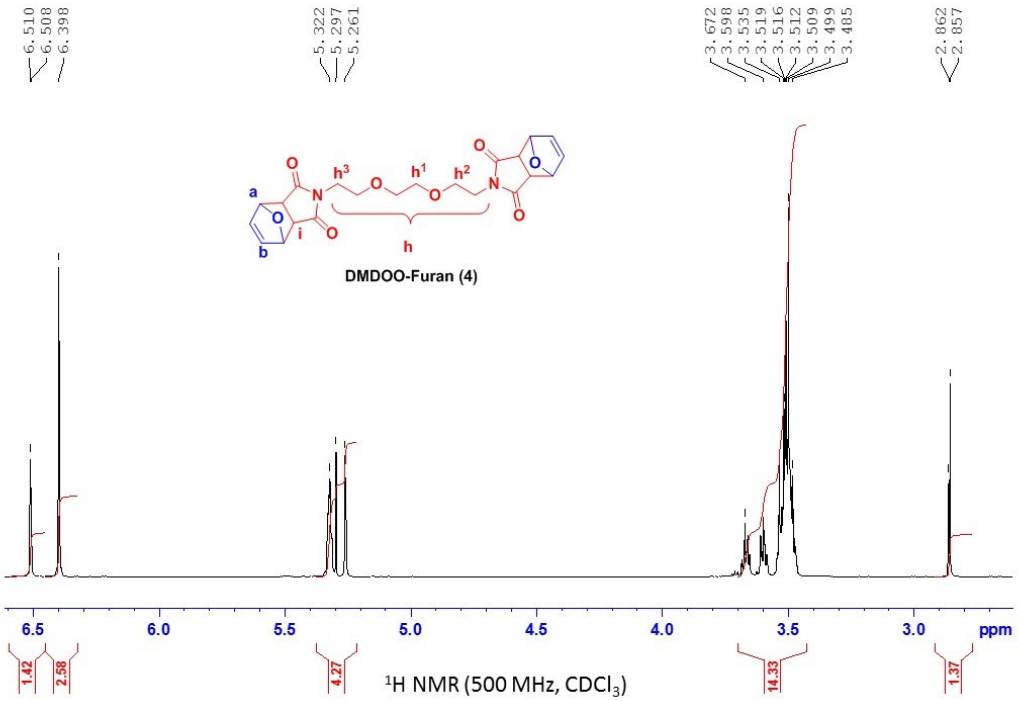
^{13}C NMR (125 MHz, DMSO-d_6)



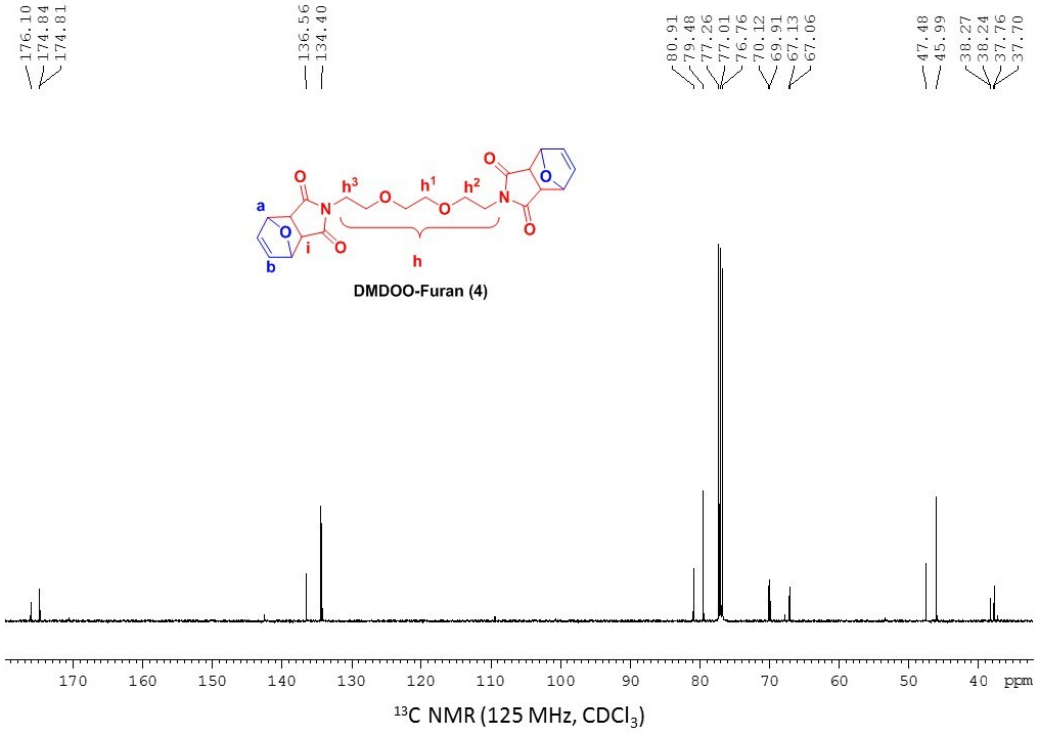
^{1}H NMR (500 MHz, DMSO-d_6)



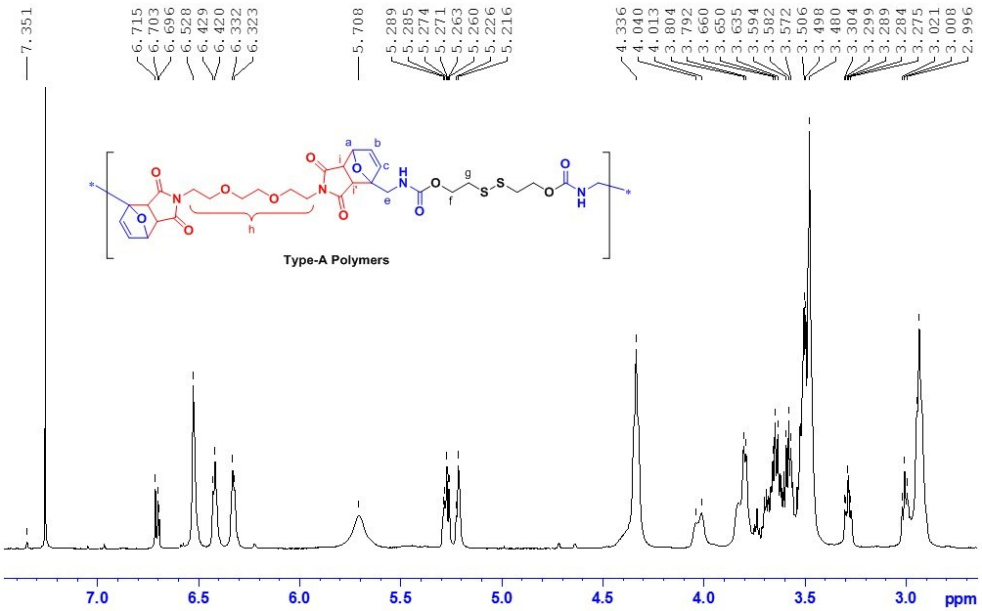
^{13}C NMR (125 MHz, DMSO-d_6)



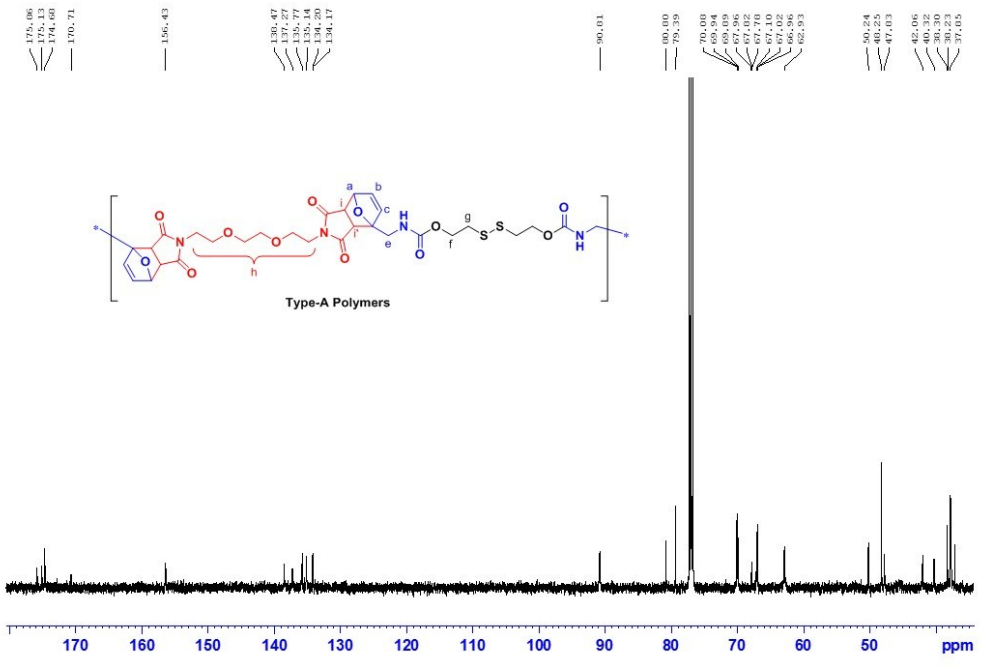
^{1}H NMR (500 MHz, $CDCl_3$)



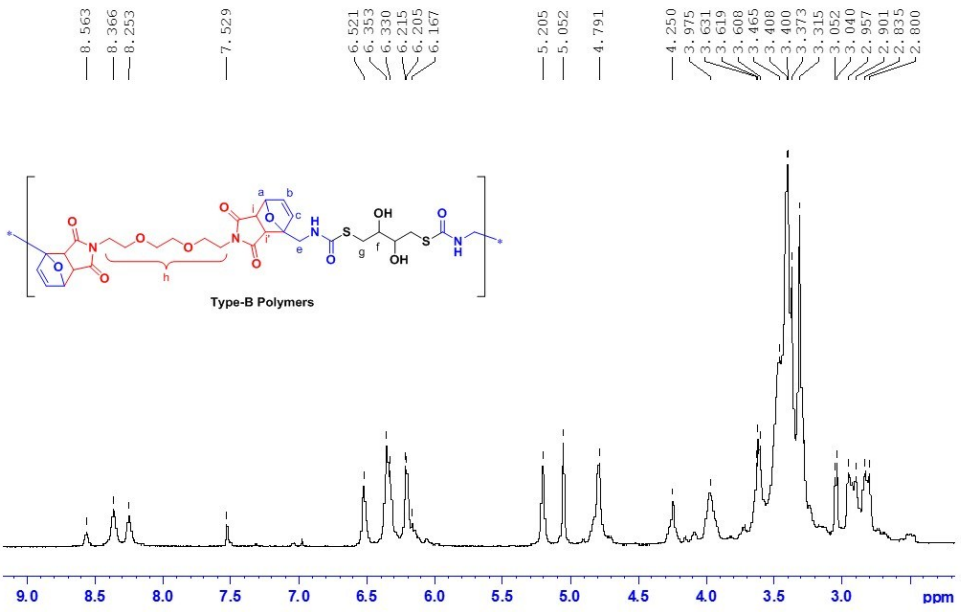
^{13}C NMR (125 MHz, $CDCl_3$)



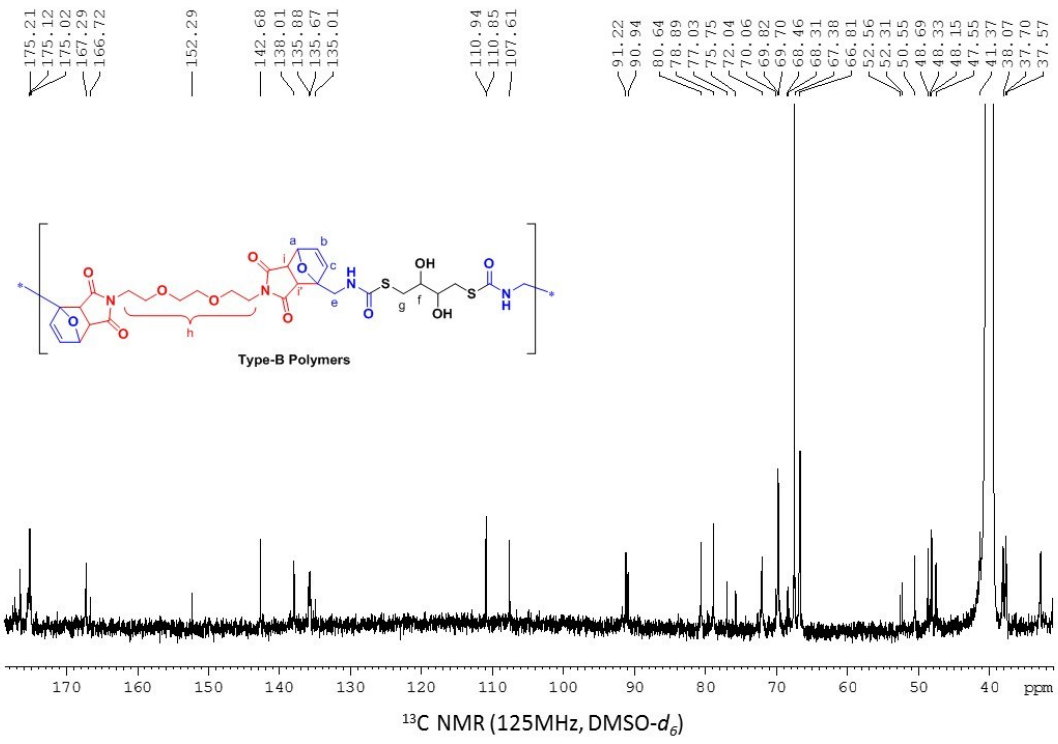
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125MHz, $CDCl_3$)

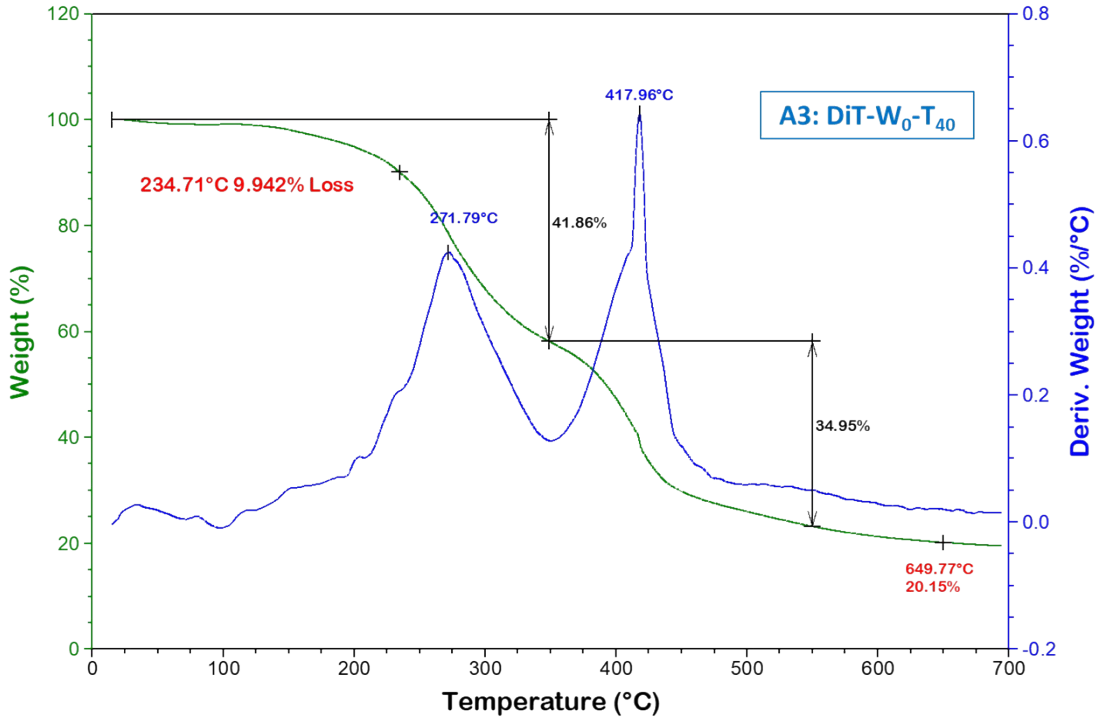


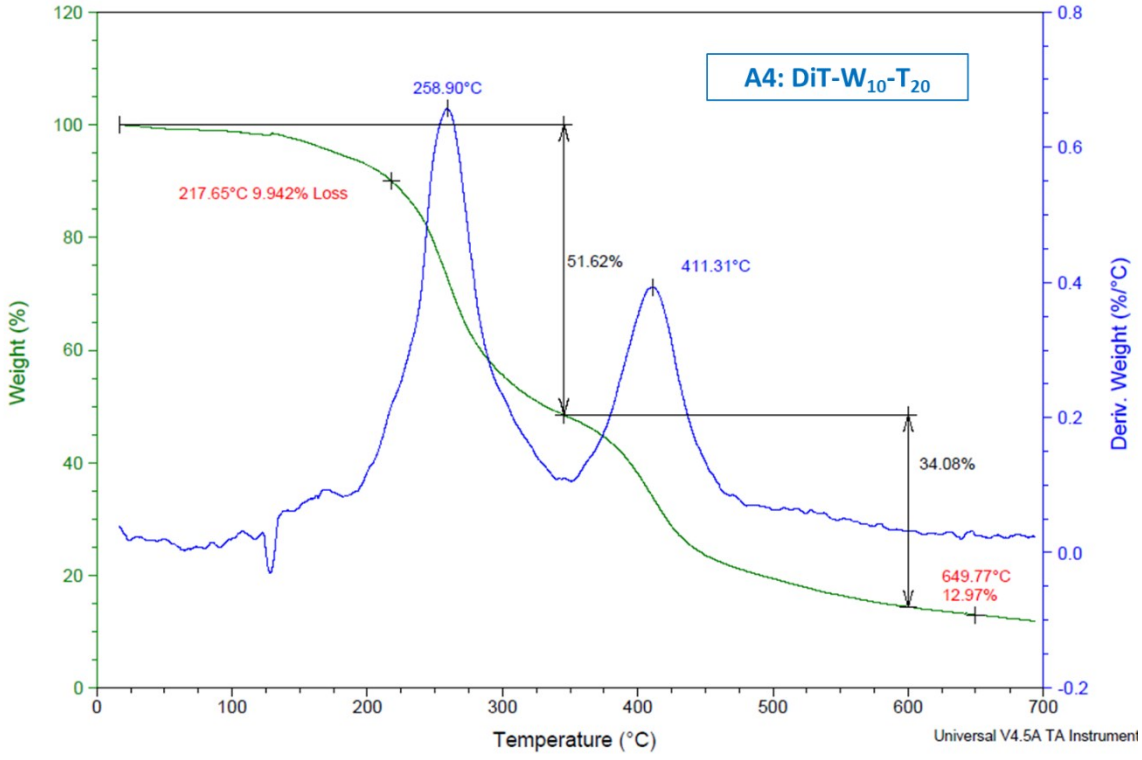
^{1}H NMR (500 MHz, DMSO-d_6)

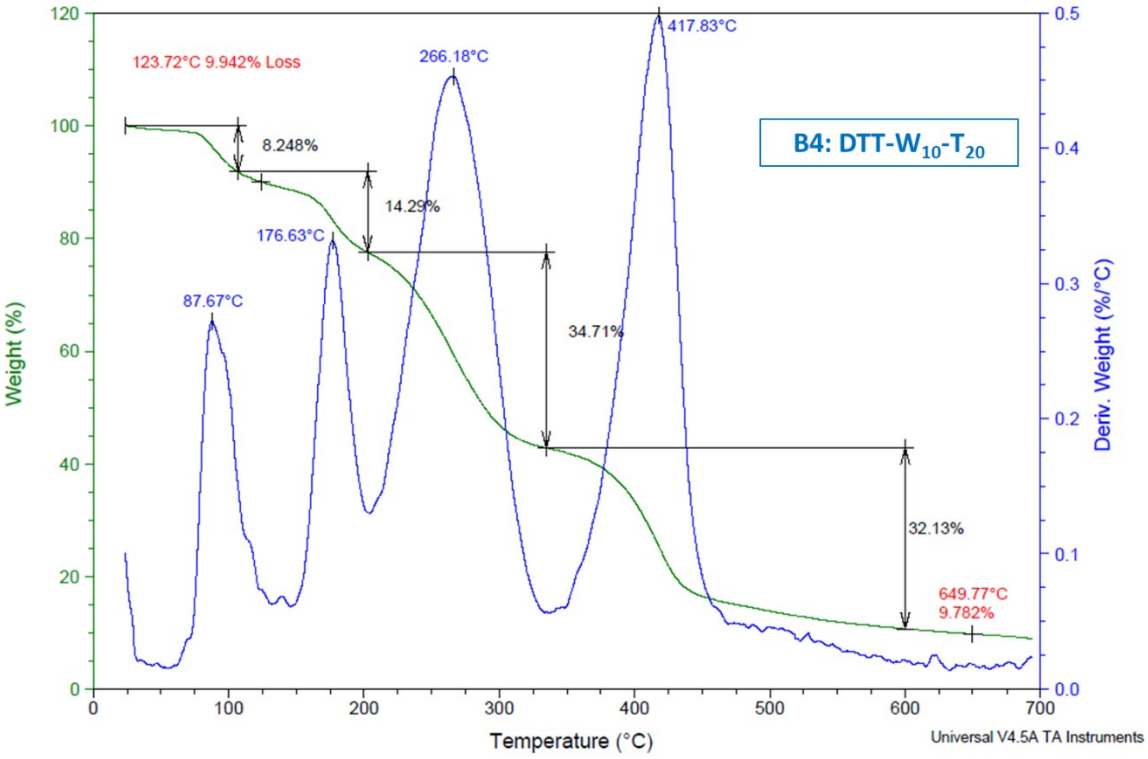


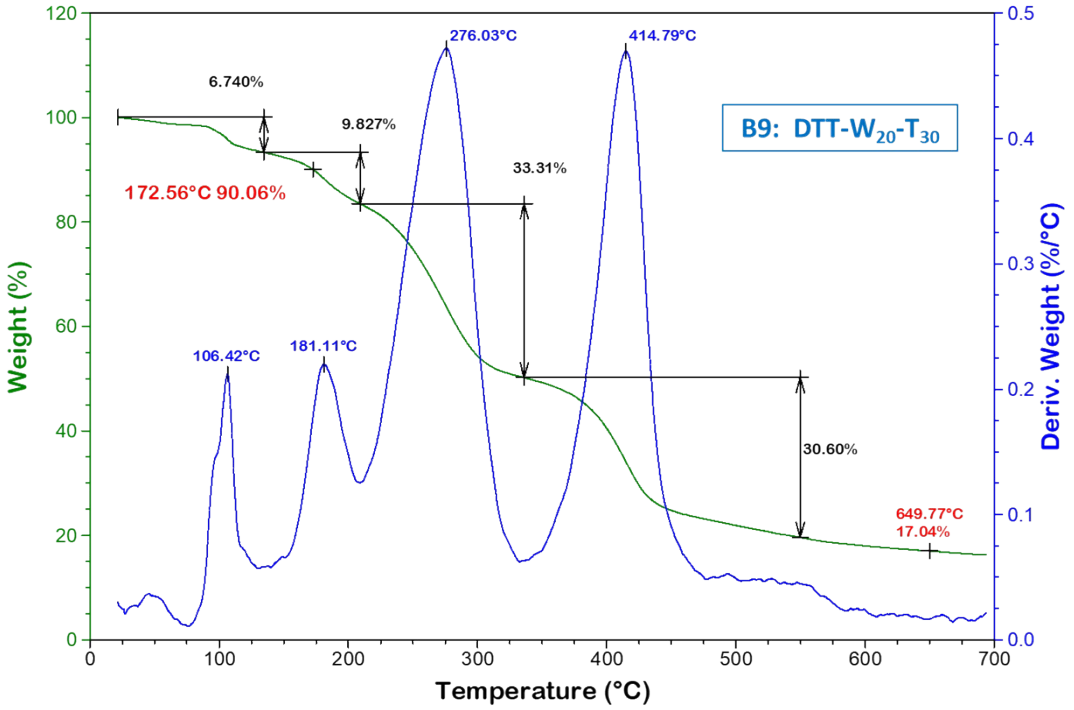
^{13}C NMR (125MHz, DMSO-d_6)

6. TGA curves

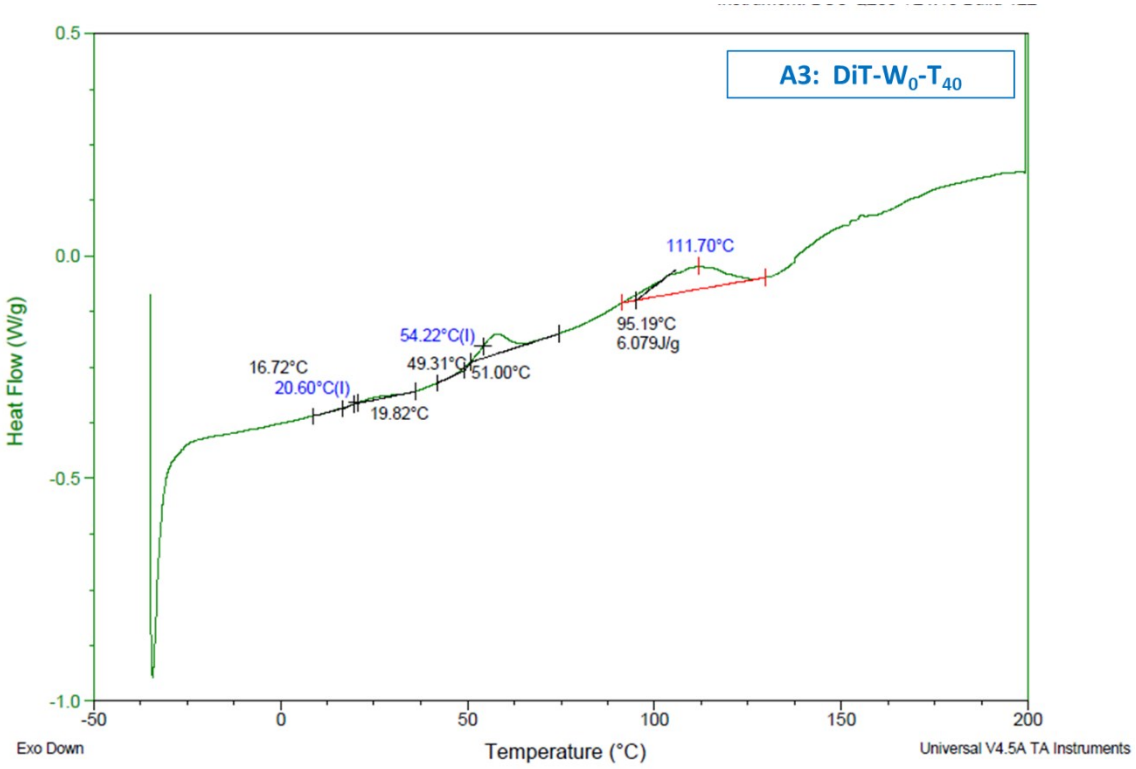

A3: DiT-W0-T40
234.71°C 9.942% Loss
271.79°C
417.96°C
41.86%
34.95%
649.77°C
20.15%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)

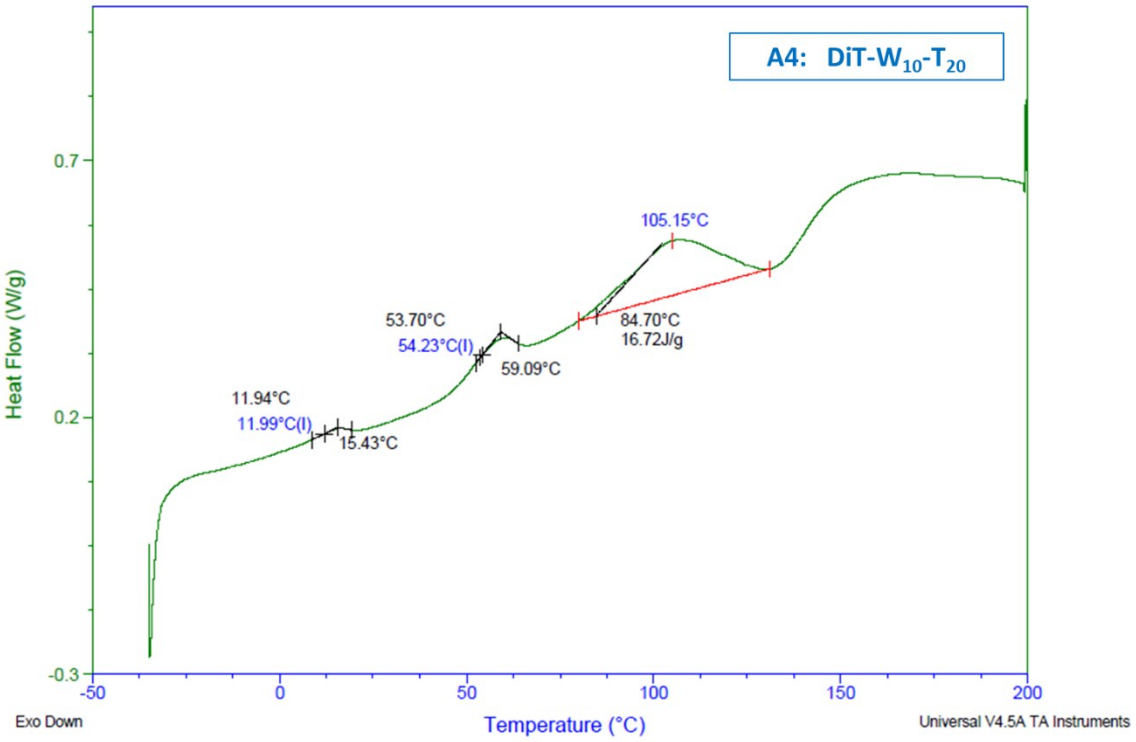

A4: DiT-W10-T20
258.90°C
217.65°C 9.942% Loss
51.62%
411.31°C
34.08%
649.77°C
12.97%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V4.5A TA Instrument

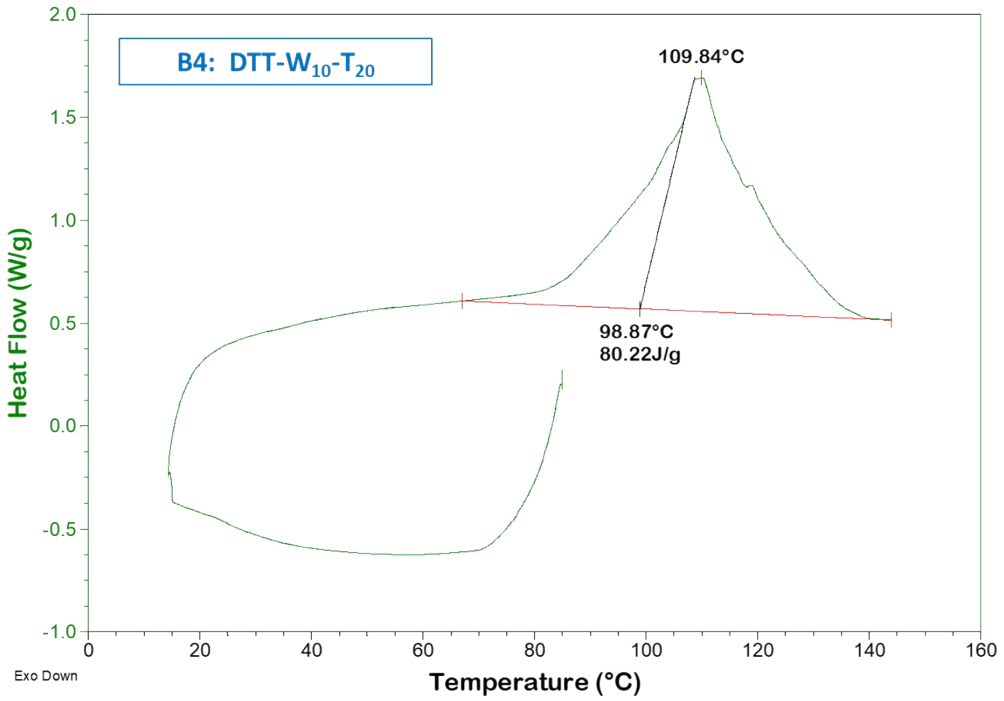

123.72°C 9.942% Loss
8.248%
14.29%
34.71%
32.13%
87.67°C
176.63°C
266.18°C
417.83°C
649.77°C
9.782%
B4: DTT-W10-T20
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V4.5A TA Instruments

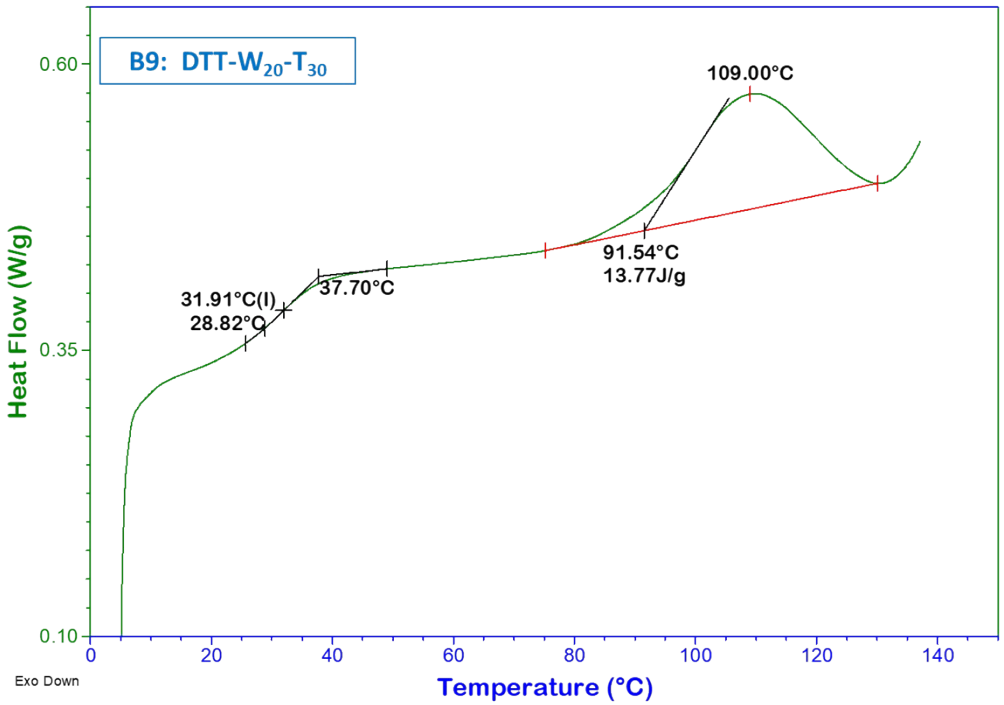

6.740%
9.827%
33.31%
30.60%
172.56°C 90.06%
106.42°C
181.11°C
276.03°C
414.79°C
649.77°C
17.04%
B9: DTT-W20-T30
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)

7. DSC curves


A3: DiT-W0-T40
Heat Flow (W/g)
0.5
0.0
-0.5
-1.0
-50
0
50
100
150
200
Temperature (°C)
Exo Down
Universal V4.5A TA Instrumentsments
111.70°C
95.19°C
6.079J/g
54.22°C(I)
49.31°C
51.00°C
16.72°C
20.60°C(I)
19.82°C


A4: DiT-W10-T20
Heat Flow (W/g)
0.7
0.2
-0.3
-50
0
50
100
150
200
Temperature (°C)
Exo Down
Universal V4.5A TA Instrumentsments
105.15°C
84.70°C
16.72J/g
53.70°C
54.23°C(I)
59.09°C
11.94°C
11.99°C(I)
15.43°C


B4: DTT-W10-T20
109.84°C
98.87°C
80.22J/g
Heat Flow (W/g)
Exo Down
Temperature (°C)


B9: DTT-W20-T30
109.00°C
91.54°C
13.77J/g
31.91°C(I)
28.82°C
37.70°C
Heat Flow (W/g)
Exo Down
Temperature (°C)