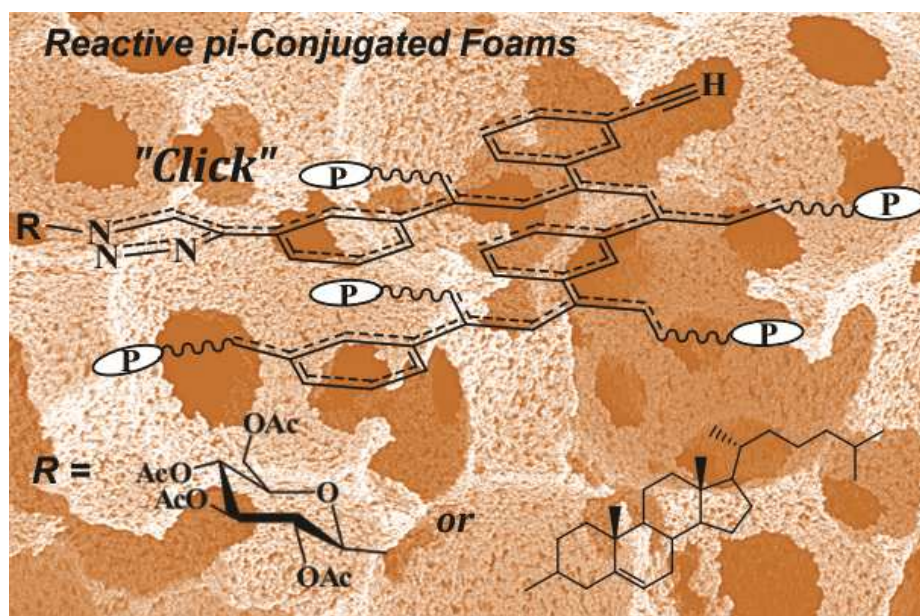


# Chain-Growth Insertion Polymerization of 1,3-Diethynylbenzene in High Internal Phase Emulsions into Reactive $\pi$ -Conjugated Foams

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## Supplementary Information



**Table S1.** Emulsions' composition

sample	V (1,3-DEB ) [mL]	m (Rh) [mg]	V (CH <sub>2</sub> Cl <sub>2</sub> ) [mL]	Surf. [mL]	V(H <sub>2</sub> O) [mL]	E <sup>a</sup> [%]	Y.P. <sup>b</sup> [%]	S <sub>BET</sub> [m <sup>2</sup> g <sup>-1</sup> ]	Skeleton density [gcm <sup>-3</sup> ] <sup>c</sup>	V <sub>micropores</sub> [cm <sup>3</sup> g <sup>-1</sup> ] <sup>d</sup>
<b>ES117</b>	2.00	44.3	1.5	0.6	17	90	66	109	1.210	0.0104
<b>ES119</b>	2.00	44.3	0.3	0.6	8	80	53	15	1.171	0.0017
<b>ES117TM</b>	Thermally modified sample ES117							387	1.300	0.1220
<b>ES119TM</b>	Thermally modified sample ES119							184	1.365	0.0114

<sup>a</sup> Theoretical porosity in per cent calculated from the volume ratio of water and 1,3-DEB<sup>b</sup> Yield of polymer<sup>c</sup> Determined by helium pycnometry<sup>d</sup> Determined from the t-plot analyses according to Harkins and Jura<sup>1</sup>

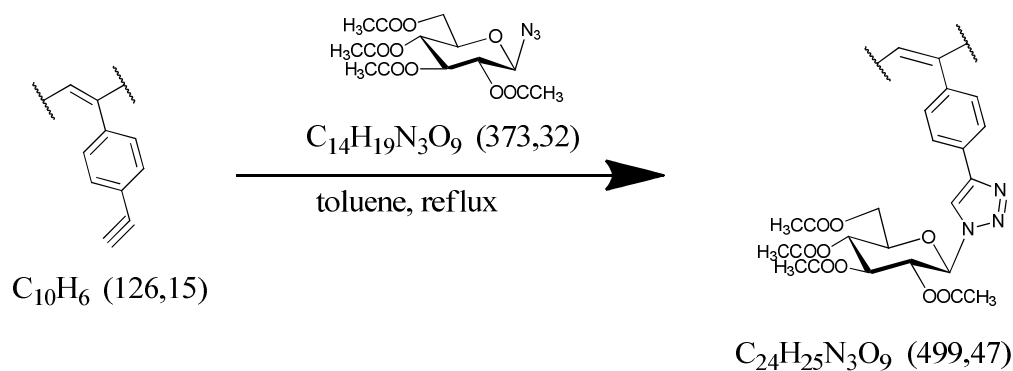
## 1. Post-modification of poly(1,3-DEB)s

### Thermal modification

Post-synthesis of poly(1,3-DEB)s was performed by thermal modification in a Büchi B-585 glass oven. Approximately 200 mg of each polymer was heated at 280°C in the glass oven for 3 h under vacuum.

### Chemical modification

#### **Preparation of ES119GLU sample**



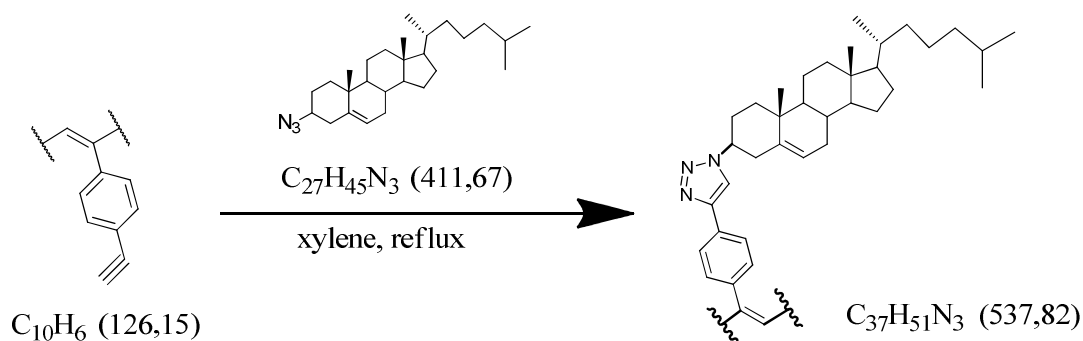
A suspension of 13 mg ES119 (ap. 0.07 mmol of ethynyl groups) and 37 mg of 1-azido-2,3,4,6-tetra-*O*-acetylglucose (GLU-N<sub>3</sub>) (0.1 mmol, 1.4 eq) in 2 ml of toluene was mixed and heated under reflux for 60 h. The obtained reaction mixture was cooled to r.t., centrifuged (9000 rpm, 8 min) and separated. The precipitate was re-suspended in 2 ml of toluene, stirred

<sup>1</sup> Jura, G.; Harkins, W. D. *J. Am. Chem. Soc.*, **1944**, 66, 1356.

for 10 min and centrifuged. The product washing was repeated with THF (2 x 2 ml) and hexane (2 x 2 ml). The solid was dried under reduced pressure to obtain 11 mg of the final product.

The degree of polymer modification was determined based on the content of nitrogen (determined by elemental analysis) assuming the above reaction stoichiometry.

### Preparation of ES119CHOL sample



A suspension of 13 mg ES119 (ap. 0.07 mmol of ethynyl groups) and 41 mg 1-azidocholesterol<sup>2</sup> (CHOL-N<sub>3</sub>) (0.1 mmol, 1.4 eq) in 2 ml of xylene was heated under reflux for 30 h. The obtained reaction mixture was cooled to r.t., centrifuged (9000 rpm, 8 min) and separated. The precipitate was resuspended in 2 ml of toluene, stirred for 10 min and centrifuged. The product washing was repeated with THF (2 x 2 ml) and hexane (2 x 2 ml). The solid was dried under reduced pressure to obtain 13 mg of the final product.

**Table S2.** Degree of substitution and loading of chemically modified ES119s

	ES119-GLU	ES119-CHOL
Degree of sub. [%]	5 <sup>a</sup>	2 <sup>b</sup>
Calcd. N [%]	1.46	0.63
Found <sup>c</sup> N [%]	1.38	0.51
Loading <sup>d</sup>	0.35	0.15

<sup>a</sup>The best value was calculated for 5 % degree of substitution; calculated values for 4 % (1.19 %) and for 6 % (1.70 %), respectively, gave higher declination from theoretical value

<sup>b</sup>The best value was calculated for 2 % degree of substitution; calculated values for 1 % (0.32 %) and for 3 % (0.91 %), respectively, gave higher declination from theoretical value

<sup>c</sup>Full elemental analysis is available in Table S3

<sup>d</sup>mmol of glucose or cholesterol groups per gram of polymer

<sup>2</sup> Sun, Q.; Cai, S.; Peterson, B. R. *Org. Lett.*, **2009**, 11(3), 567

## 2. Elemental Analysis (EA)

Elemental analyses of the polymers were performed at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic.

**Table S3.** Elemental analysis data

Sample	C [w%]	H [w%]	N [w%]
ES119	90.96	4.52	-
ES119TM	86.71	3.77	-
ES119-GLU	79.71	6.48	1.38
ES119-CHOL	79.94	5.18	0.51
ES117	91.39	4.25	-
ES117TM	83.75	3.34	-

The finding that the total mass of C and H (by elemental analysis, EA) is below 100 % in the case of purely hydrocarbon polymers can be a consequence of (i) an incomplete combustion of the polymers during EA and/or (ii) (to a lesser extent) polymer contamination with (insoluble) Rh catalyst residue. Similar differences between the calculated and (by combustion EA) found elemental compositions have been reported for various hypercross-linked polymers that are rich in aromatic units and multiple bonds.<sup>3</sup>

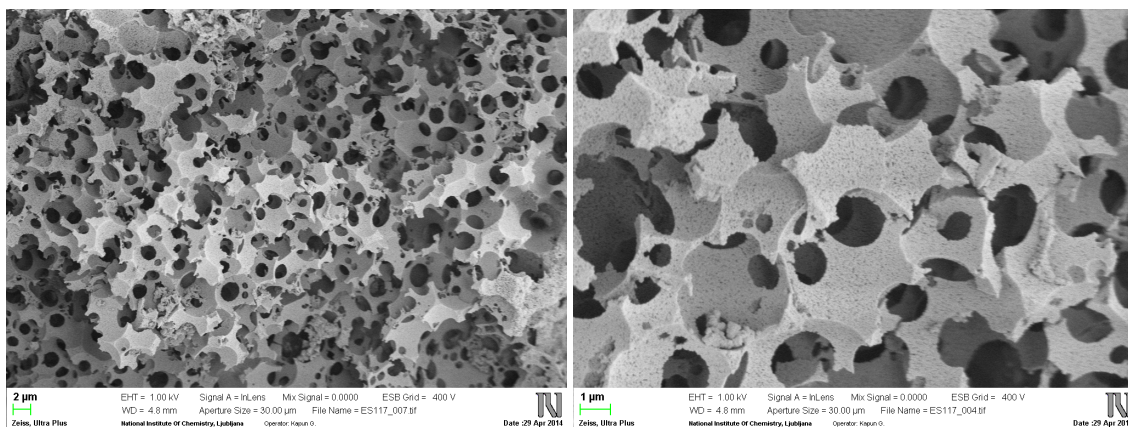
## 3. Characterization

### 3.1. Scanning electron microscopy (SEM)

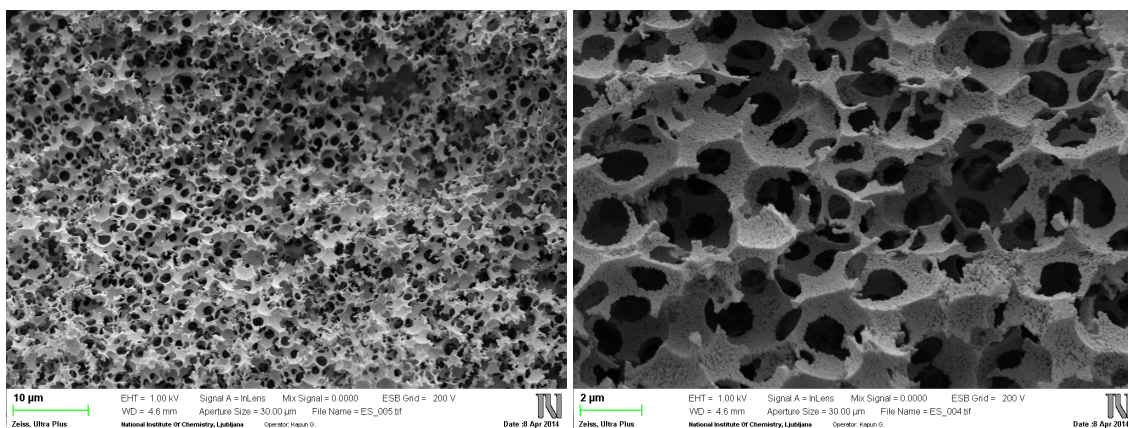
Morphology investigations were performed by a scanning electron microscopy. SEM images were taken on a Field emission electron microscope Ultra+ (Carl Zeiss) equipped with an energy dispersive spectrometer SDD X-Max 50 (Oxford Instruments). A piece of each sample was mounted on a carbon tab for better conductivity and a thin layer of gold was sputtered on sample surface prior scanning analysis. An average void size was determined from SEM micrographs analysis after scanning. Therefore, the mean and the standard deviations were drawn by manual measurements of diameters from a population of at least 40 voids. From SEM images analysis it is difficult to give a correct evaluation of the void size since the pores are inside the material and during the sample sectioning the cavities which appear are at

<sup>3</sup> (a) Jiang, J.-X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z.; Cooper, A. I. *Angew. Chem. Int. Ed.*, **2007**, 46, 8574–8578. (b) Holst, J. R.; Stöckel, E.; Adams, D. J.; Cooper, A. I. *Macromolecules*, **2010**, 43, 8531–8538.

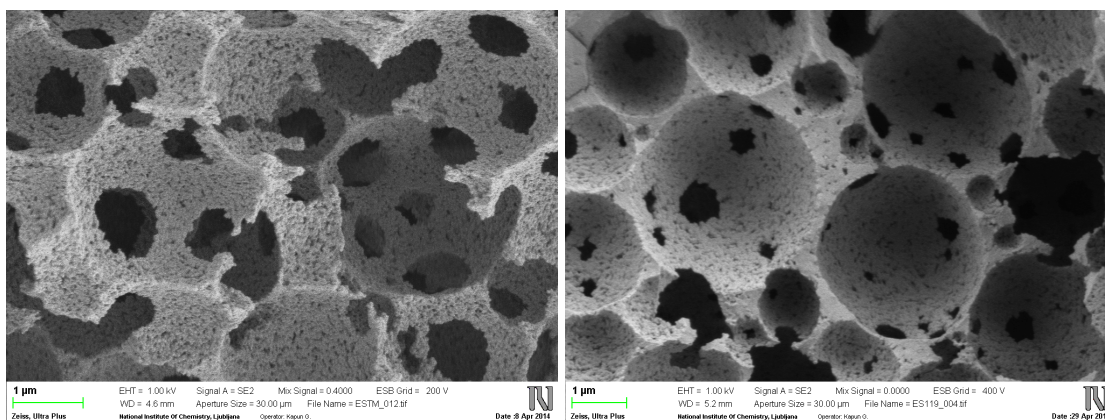
random distance from the cavity centre. To get a better estimation of the real void diameter, it is necessary to introduce a statistical correction. Multiplication of the observed voids values from SEM images by a statistical factor of  $2/3^{1/2}$  allows for a better estimation of the real cavity diameters.<sup>4</sup>



**Figure S1.** SEM images of sample ES117.



**Figure S2.** SEM images of sample ES119.

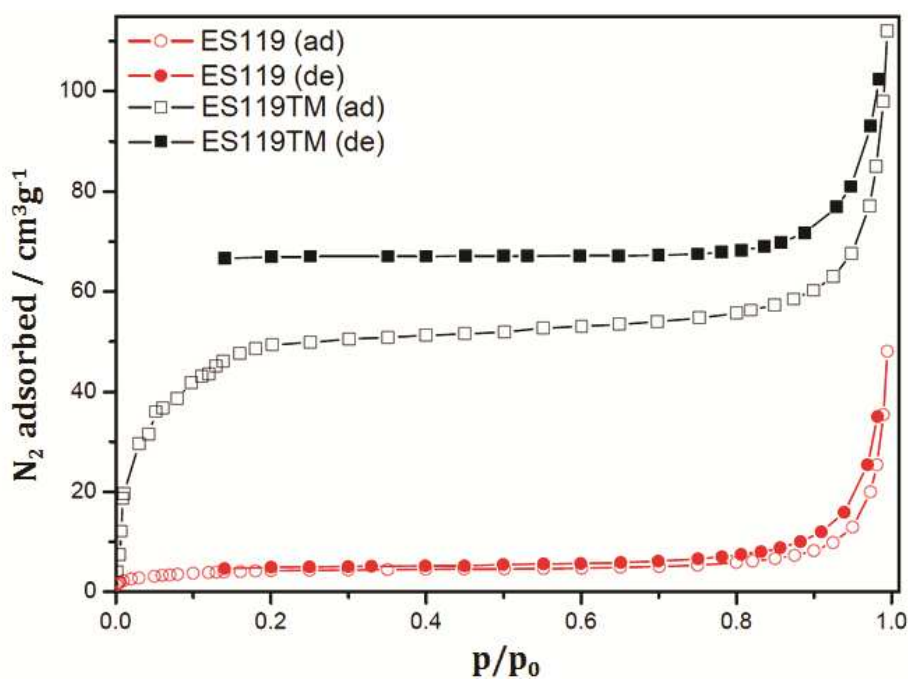


<sup>4</sup> A. Barbetta and N. R. Cameron, *Macromolecules*, 2004, **37**, 3188-3201

**Figure S3.** SEM images of thermally modified sample ES119TM (left) and chemically modified sample ES119CHOL (right).

### 3.2. BET (Brunauer-Emmett-Teller) surface area

Nitrogen adsorption measurements of polymer samples were performed on a Micromeritics TriStar 3000 surface area analyzer. The samples were outgassed at 90°C under turbomolecular pump vacuum. The BET surface area was determined by means of nitrogen adsorption data in relative pressure range from 0.05 to 0.25. The BET transform plots were linear in this pressure range.



**Figure S4.**  $N_2$  adsorption/desorption isotherms (77 °K) on ES119 and ES119TM samples.



### 3.3. Fourier Transform IR (FTIR) Spectroscopy

FTIR spectra were measured on a Nicolet Magna IR 760 using a diffuse reflection mode (DRIFTS). Samples were diluted with KBr.

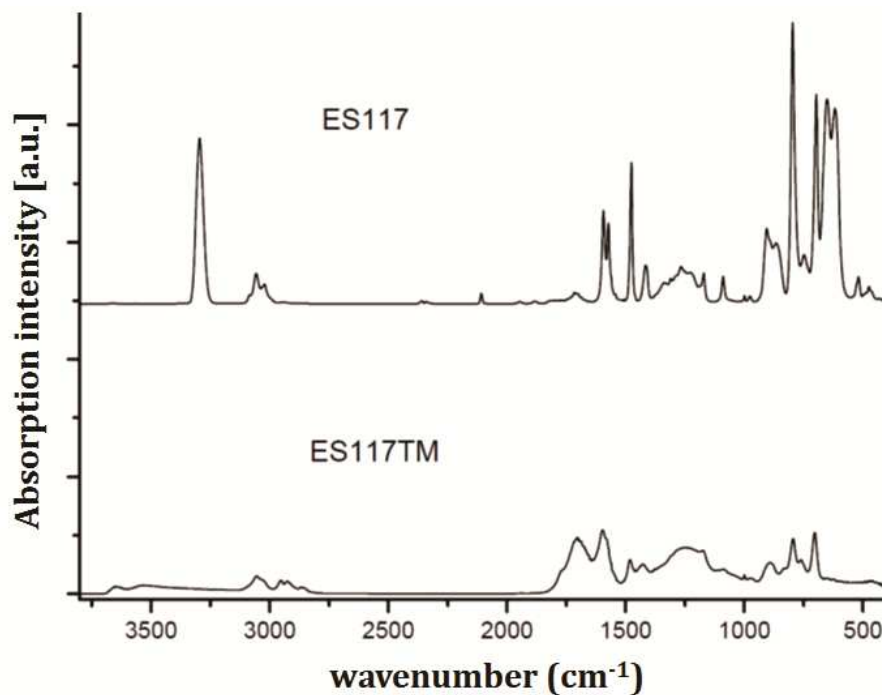


Figure S5. FTIR spectra of pristine ES117 and thermally modified ES117TM samples.

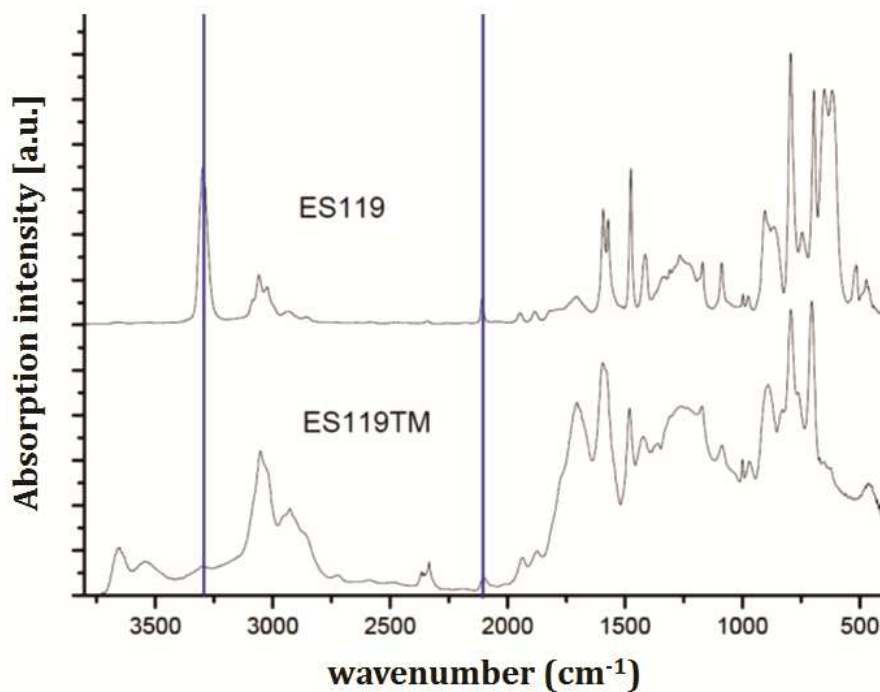
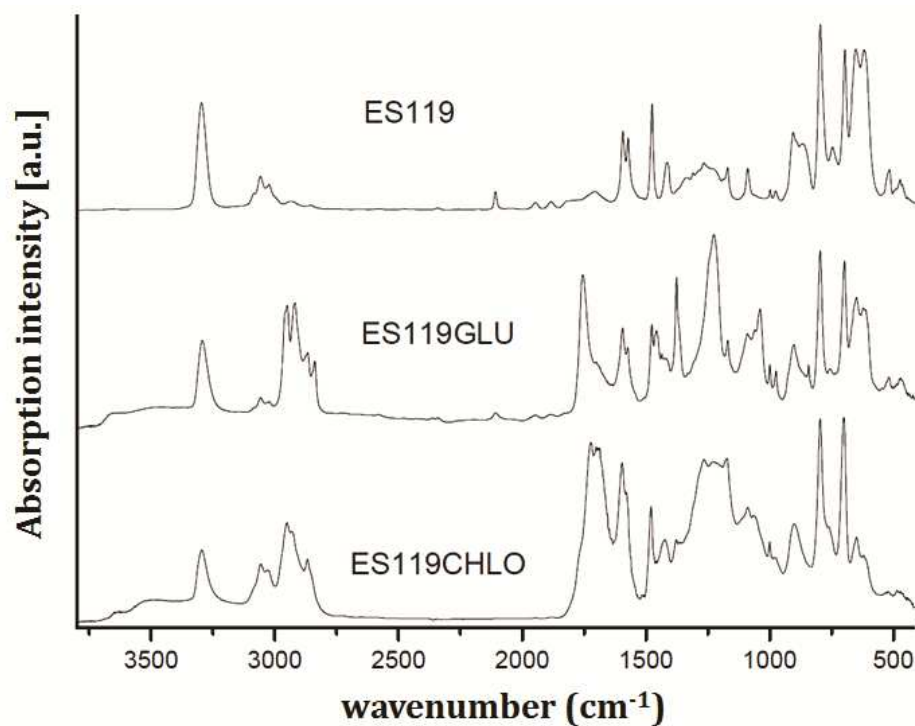


Figure S6. FTIR spectra of pristine ES119 and thermally modified ES119TM samples.

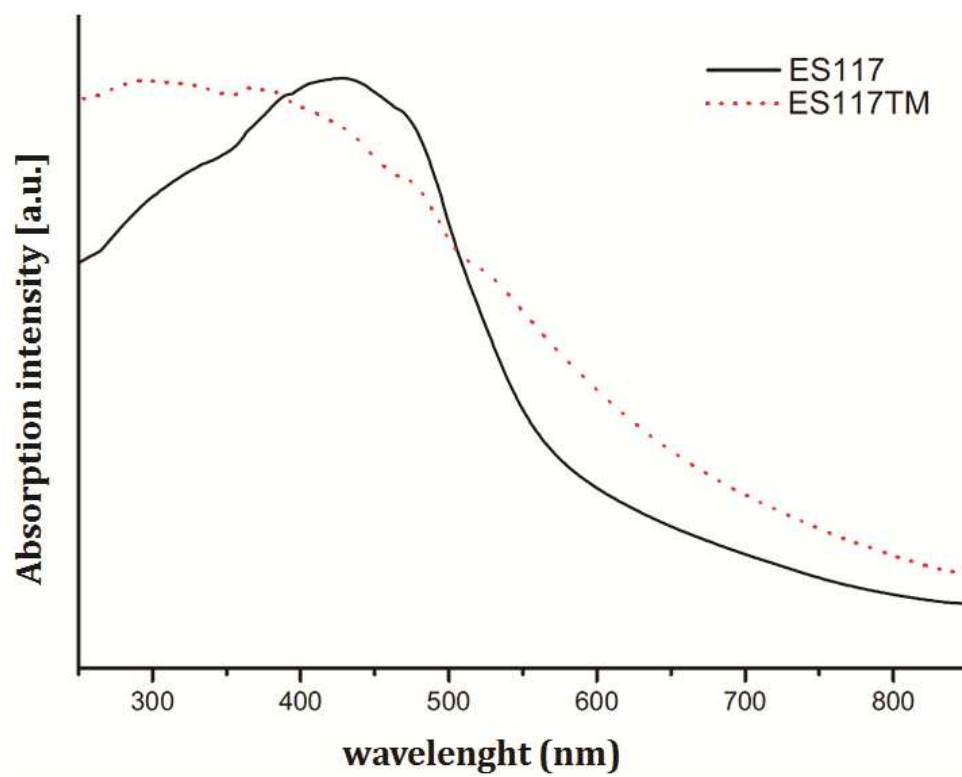


**Figure S7.** FTIR spectra of pristine ES119 and chemically modified ES119GLU and ES119CHOL samples.

### **3.4. Diffuse reflectance UV/vis spectroscopy (DR UV/vis)**

Diffuse Reflectance UV/vis (DR UV/vis) spectra of solid polymers were recorded using a Perkin–Elmer Lambda 950 spectrometer. Before DR UV/vis measurements the polymers were diluted with BaSO<sub>4</sub> (1/10, w/w).





**Figure S8.** DR UV/vis spectra of pristine ES117 and thermally modified ES117TM samples.