

## Supporting Information

### Polymerization-Induced Clusteroluminescence of Poly(cyclic carbonate)s

Bin Liu,<sup>\*a,b</sup> Genghong Huang,<sup>a</sup> Hu-liang Lu,<sup>c</sup> Kang Chen,<sup>c</sup> Zishan Yan,<sup>c</sup> Ya-Ling Wang,<sup>a</sup> Bo Chu,<sup>b</sup> Fu-de Ren,<sup>e</sup> Yongzhen Yang,<sup>c,d</sup> and Xing-Hong Zhang<sup>b\*</sup>

<sup>a</sup>School of Energy and Power Engineering, North University of China, Taiyuan 030051, P. R. China. E-mail: liubin@nuc.edu.cn

<sup>b</sup>MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: xhzhang@zju.edu.cn

<sup>c</sup>MOE Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Taiyuan 030024, P. R. China.

<sup>d</sup>Shanxi-Zheda Institute of Advanced Materials and Chemical Engineering, Taiyuan 030032, P. R. China.

<sup>e</sup>School of Chemical Engineering and Technology, North University of China, Taiyuan 030051, P. R. China.

#### Experimental section

**Materials:** vinylene carbonate (VC, 99%, J&K) and vinyl ethylene carbonate (VEC, 99%, J&K) were purified by vacuum distillation. 2, 2'-azobisisobutyronitrile (AIBN, 99%, J&K) was obtained by recrystallization. Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), dioxane, propylene carbonate (PC) and ethylene carbonate (EC) were spectrally pure and purchased from Aladdin. Deionized water was used in all the experiments.

**Characterization:** photoluminescence (PL) spectra were collected from an FS5 spectrometer with a 150 W xenon arc excitation source. The fluorescence decay curve was recorded on an Instruments FLS980 transient spectrometer. Absolute quantum yields ( $\Phi_f$ ) were obtained by integrating sphere with an excitation wavelength ( $\lambda_{ex}$ ) of 360 nm. Proton (<sup>1</sup>H NMR) and Carbon-13 nuclear magnetic resonance spectroscopy spectra (<sup>13</sup>C NMR) were performed on a Bruker Advance DMX 400 MHz instrument. The number-averaged molecular weight ( $M_n$ ) and molecular weight distribution ( $D = M_w/M_n$ ) were determined using a Waters 2414 refractive index (RI) detection system equipped with a Waters 1525 isocratic HPLC pump. The gel permeation chromatography (GPC) columns were eluted with dimethylformamide with 1.0

mL/min at 60 °C. The sample concentration was 0.4 wt %, and the injection volume was 100  $\mu$ L. Calibration was performed using monodisperse polymethyl methacrylate (PMMA) standards. Differential scanning calorimetry (DSC) tests were conducted on a TA Instruments TA-Q200 instrument (New Castle, DE) at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere, and the data from the second heating curve was collected. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer Pyris TMS 1 thermogravimetric analyzer from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. The morphologies of fibers, microspheres and sponges were studied by a Zeiss LEO 1530 (Gemini, Germany) scanning electron microscope (SEM). The diameter of the microspheres was measured by dynamic light scattering (DLS) at a scattering angle  $\theta = 90^\circ$  as a function of temperature using a 90 Plus Particle Size Analyzer. Fourier transform infrared (FT-IR) spectroscopy was performed on a Bruker TENSOR 27 spectrometer.

**Synthesis of poly(vinylene carbonate) (PVC):** PVC with high  $M_n$  was prepared by bulk polymerization of VC.<sup>1</sup> VC (3 mL, 47.4 mmol) and AIBN (29.5 mg, 0.18 mmol) were transferred into a 20 mL three-necked flask and reacted at 70 °C for 2.4 min under N<sub>2</sub> atmosphere. Then DMF was added into the three-necked flask to dissolve the crude product. The resulting PVC was purified by three precipitations in excess methanol followed by vacuum drying at 60 °C to constant weight. The  $M_n$  and  $\bar{D}$  of PVC are 1436.7 KDa and 2.0, respectively.

PVC with relatively low  $M_n$  was prepared by solution polymerization of VC. VC (2.5 mL, 39.5 mmol), AIBN (64.8 mg, 0.39 mmol) and dioxane (10 mL) were transferred into a 20 mL three-necked flask and reacted at 65 °C for 17 h under N<sub>2</sub> atmosphere. The crude PVC dioxane solution was precipitated in excess methanol and washed in methanol for three times. Finally, the pure white PVC powder was vacuum-dried at 60 °C to constant weight. The  $M_n$  and  $\bar{D}$  of PVC are 8.3 KDa and 1.7, respectively. The  $M_n$  of PVC can be controlled by adjusting the ratio of VC and AIBN. When the mole ratio of VC and AIBN is 220:1, 40:1 and 30:1, the corresponding  $M_n$  and  $\bar{D}$  of PVC are 18.8 KDa/1.8, 3.3 KDa/1.6 and 2.5 KDa/1.3, respectively.

**Preparation of PVC electrospun fibers:** a series of PVC/DMF solutions with different concentration (25 wt%, 27 wt%, 29 wt%, 31 wt%, 33 wt%, 35 wt%) were prepared. Then, the solution was loaded into a syringe

capped with a metal needle (diameter: 0.6 mm). The feed rate of 0.8 mL h<sup>-1</sup> was controlled by a syringe pump. Continuous electrospun fibers were deposited on tin foil after applying a positive DC voltage of 19.9 kV to the syringe needle. The tip-to-collector distance was about 25 cm. After electrospinning, the fibers were vacuum-dried at 60 °C to constant weight.

**Preparation of PVC electrospay microspheres:** PVC/DMF solutions with a concentration of 15 wt% was formulated and loaded into a syringe capped with a metal needle (diameter: 0.6 mm). The feed rate of 0.8 mL h<sup>-1</sup> was controlled by a syringe pump. The metal needle was connected to a positive DC voltage of 19.9 kV and positioned about 10 cm above the water surface.

**Preparation of PVC sponge:** a high concentration PVC/DMF solution was prepared by dissolving pure PVC in DMF, and precipitated dropwise in excess methanol. Owing to the large  $M_n$ , cotton-like white flocculent PVC was precipitated. After being fully stirred and filtered in a Buchner funnel, dispersed in water and dried in vacuum, PVC sponge was prepared.

**Synthesis of poly(vinylethylene carbonate) (PVEC):** VEC (2.50 g, 21.93 mmol) and AIBN (12.1 mg, 0.074 mmol) were transferred into a 10 mL three-necked flask and reacted at 70 °C for 12 h under N<sub>2</sub> atmosphere.<sup>2</sup> The resulting PVEC was purified by precipitations three times in excess methanol followed by vacuum drying at 60 °C to constant weight. The  $M_n$  and  $\bar{D}$  of PVEC are 8.5 KDa and 2.0, respectively.

**Computational details:** all geometric optimizations were performed using the TD-DFT method at the B3LYP/6-31(d) level using the Gaussian 09 procedure. The distances of oxygen atoms in the polymers were determined using Gaussian view 6.0.

## Results and discussion

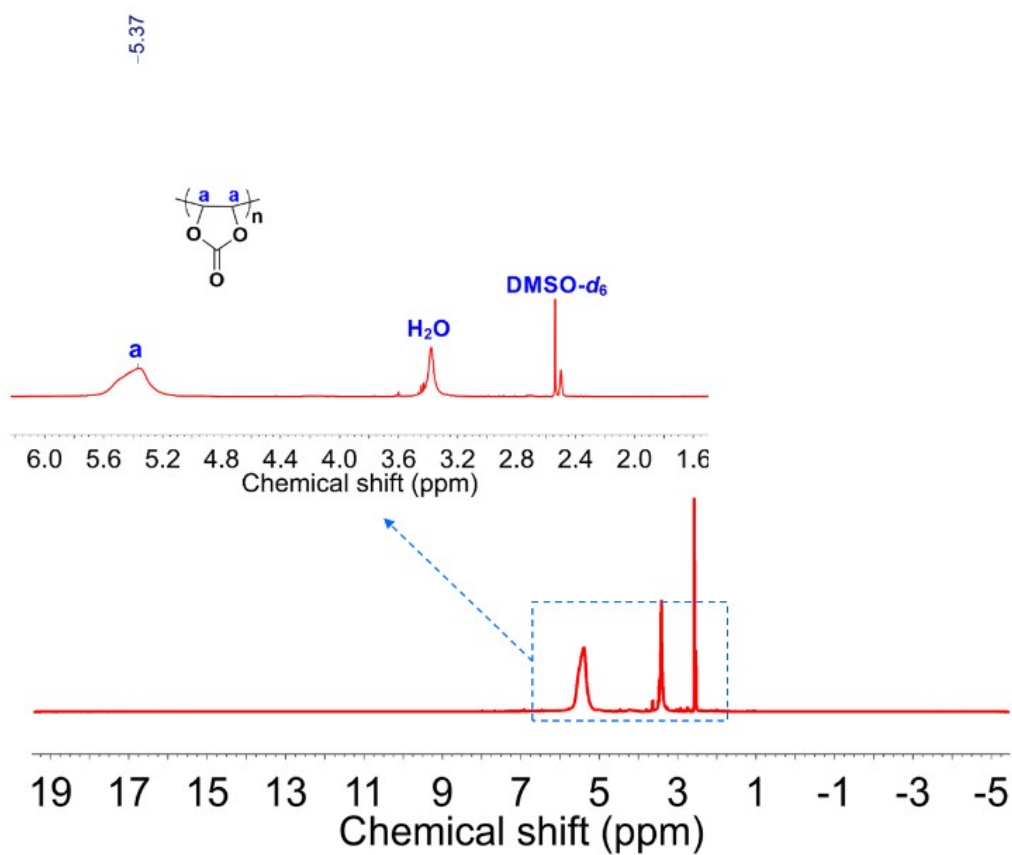


Figure S1.  $^1\text{H}$  NMR spectrum of PVC.

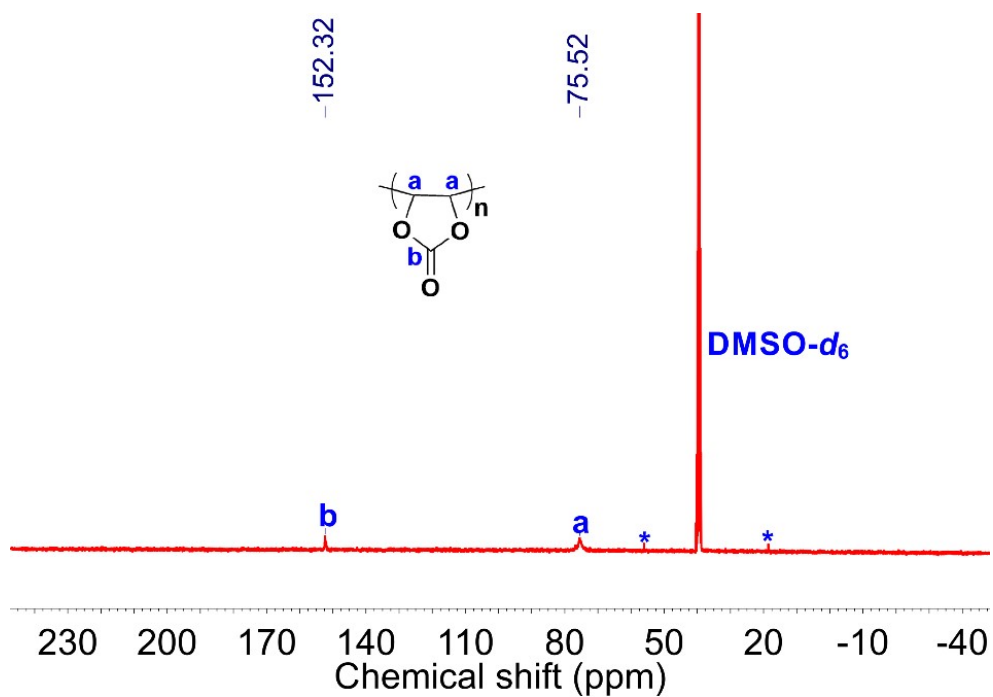


Figure S2.  $^{13}\text{C}$  NMR spectrum of PVC.

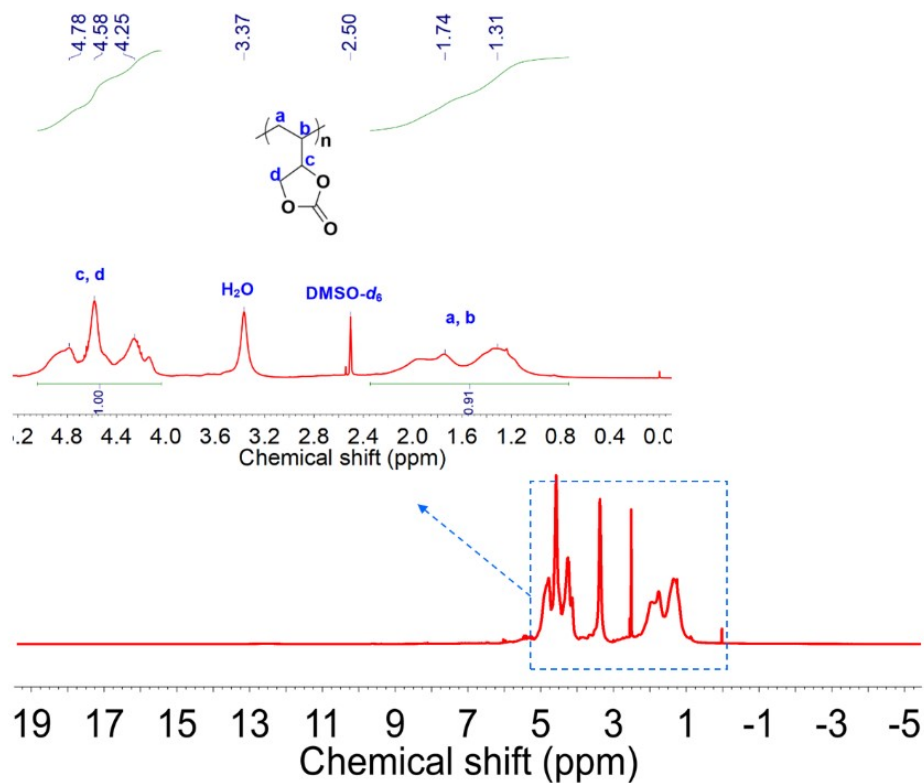


Figure S3.  $^1\text{H}$  NMR spectrum of PVEC.

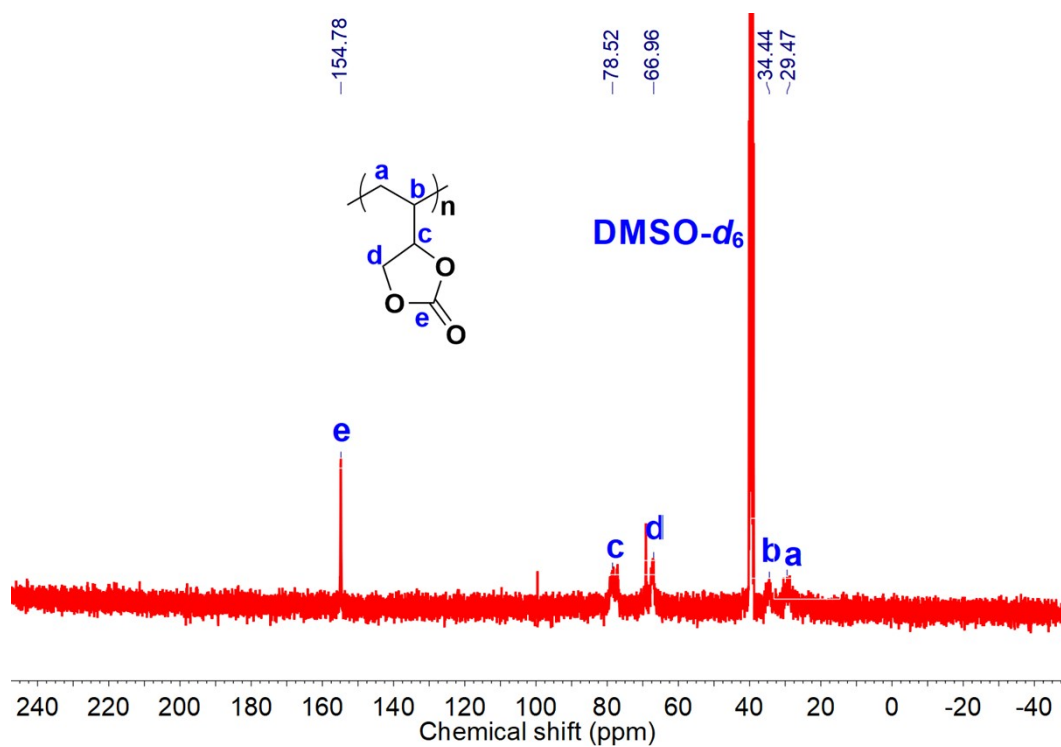


Figure S4.  $^{13}\text{C}$  NMR spectrum of PVEC.

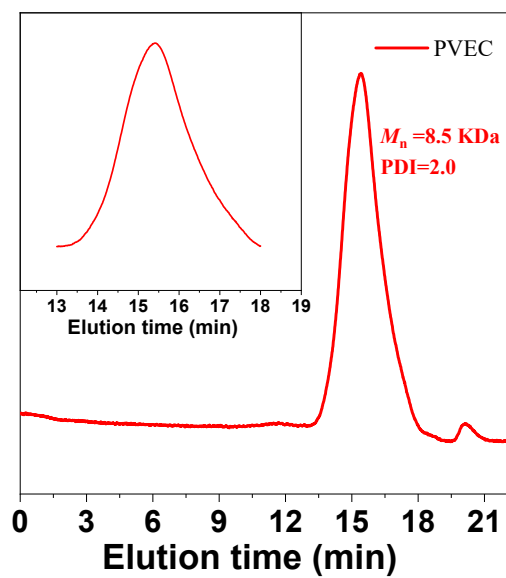


Figure S5. GPC curve of PVEC.

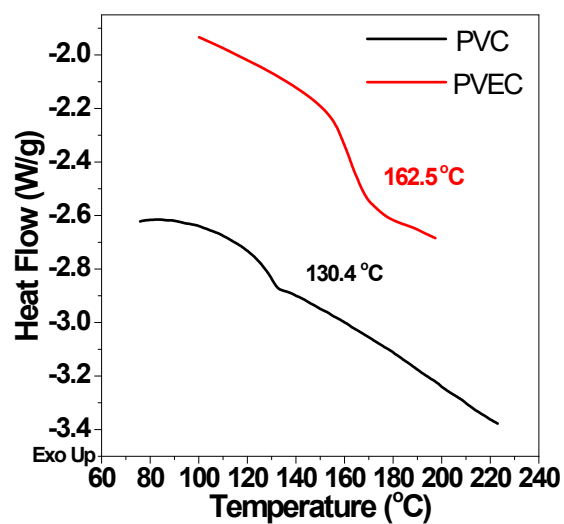
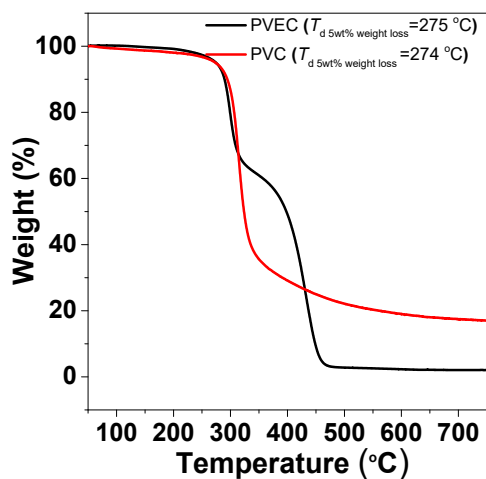
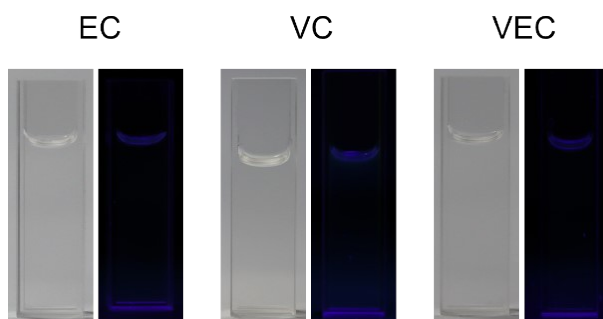


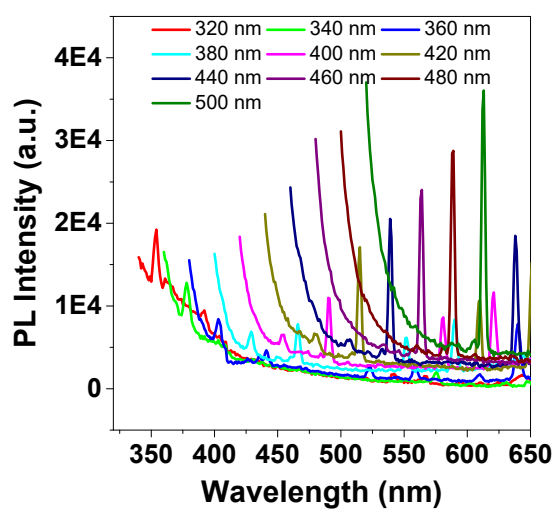
Figure S6. DSC curves of PVEC ( $M_n = 8.5$  KDa,  $\bar{D} = 2.0$ ) and PVC ( $M_n = 1436.7$  KDa,  $\bar{D} = 2.0$ ).



**Figure S7.** TGA curves of PVEC ( $M_n = 8.5$  KDa,  $\bar{D}=2.0$ ) and PVC ( $M_n = 1436.7$  KDa,  $\bar{D}=2.0$ ).



**Figure S8.** Photographs of EC, VC and VEC taken in daylight (left) and under 365 nm UV irradiation (right).



**Figure S9.** PL spectra of pure EC at different  $\lambda_{ex}$ .

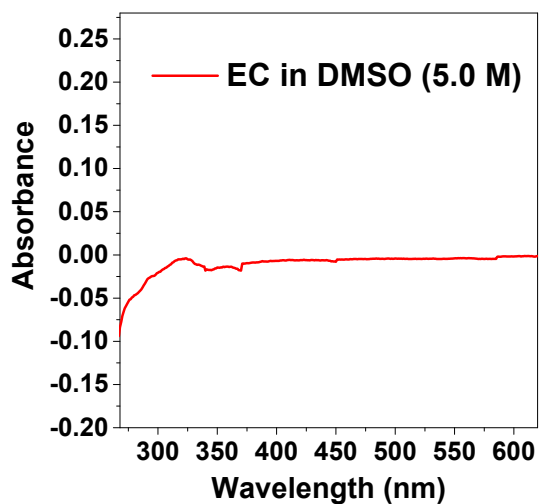


Figure S10. UV-vis absorption spectra of EC in DMSO (5.0 M).

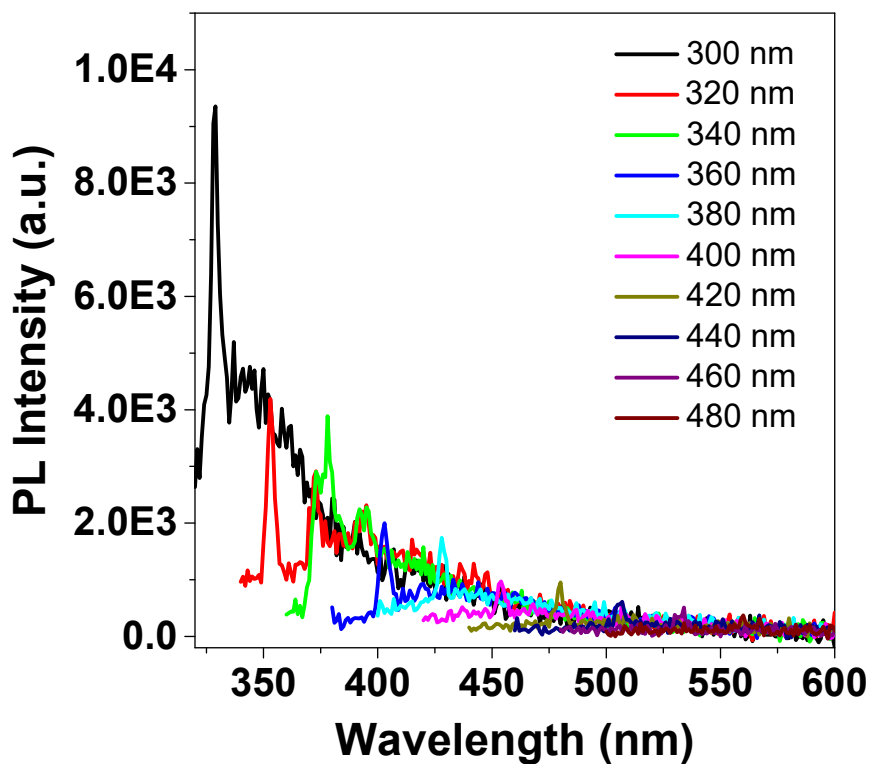
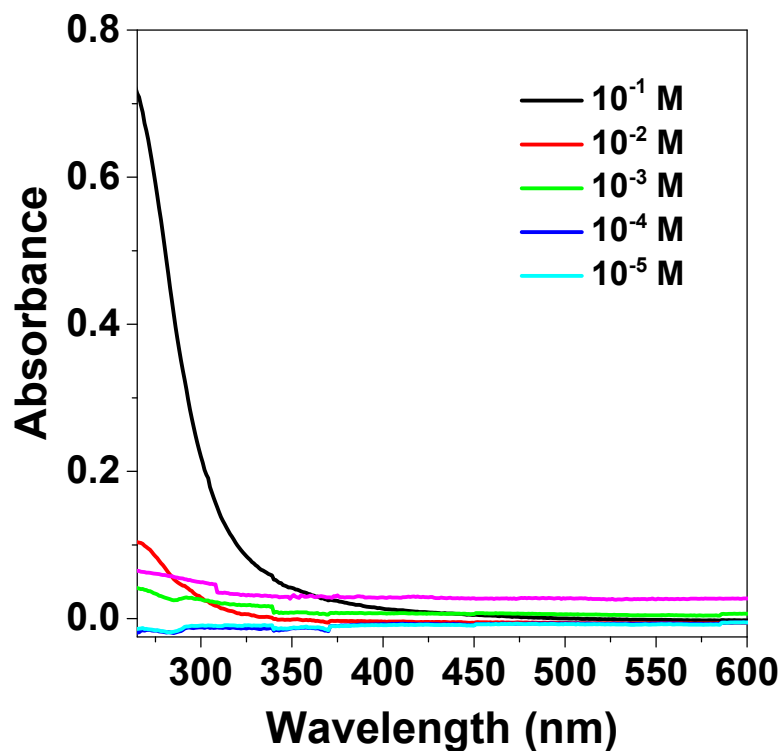
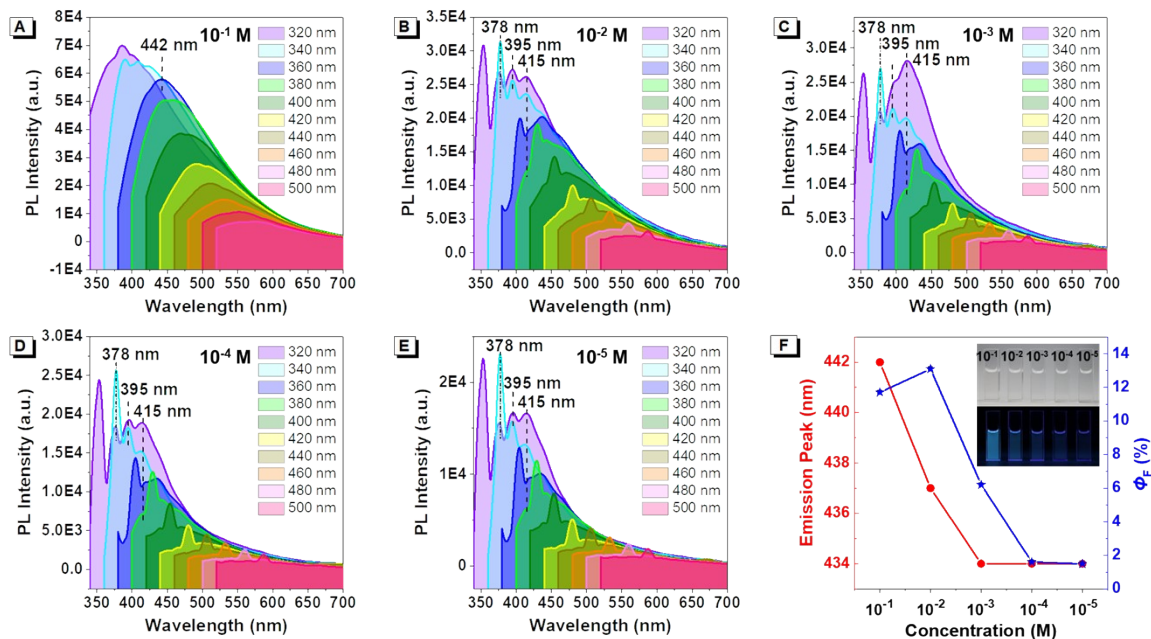


Figure S11. PL spectra of pure DMSO at different  $\lambda_{\text{ex}}$ .

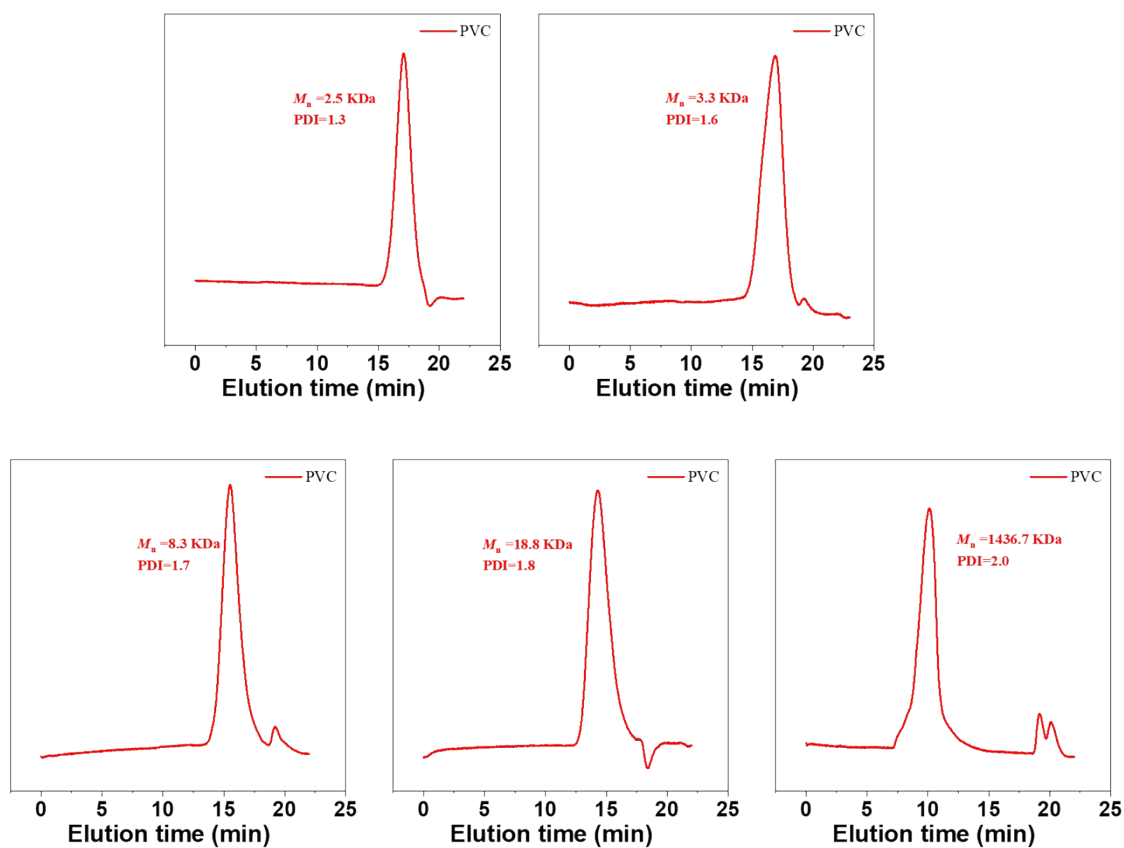




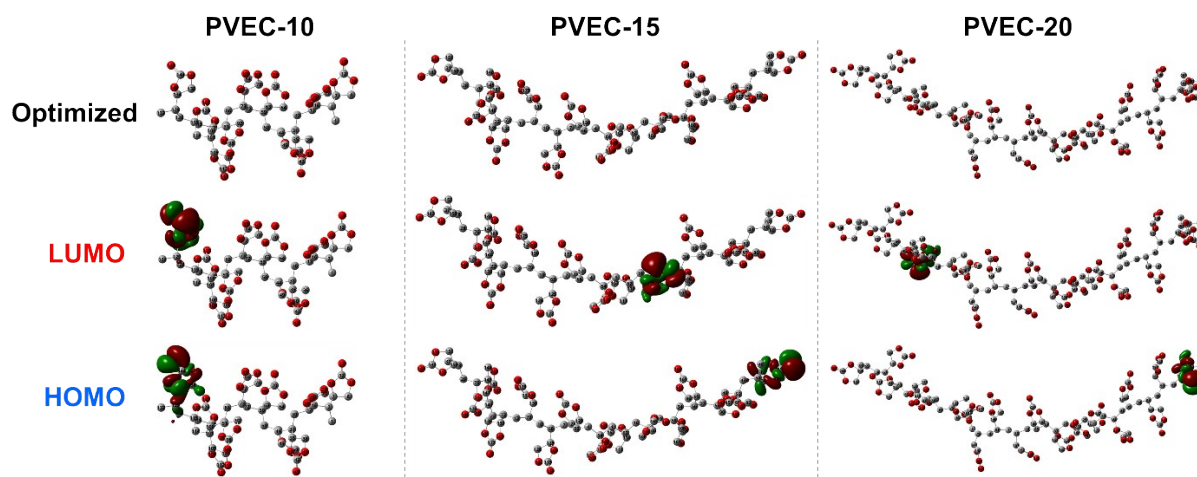
**Figure S12.** UV-vis absorption spectra of PVEC/DMSO solutions with different concentrations.



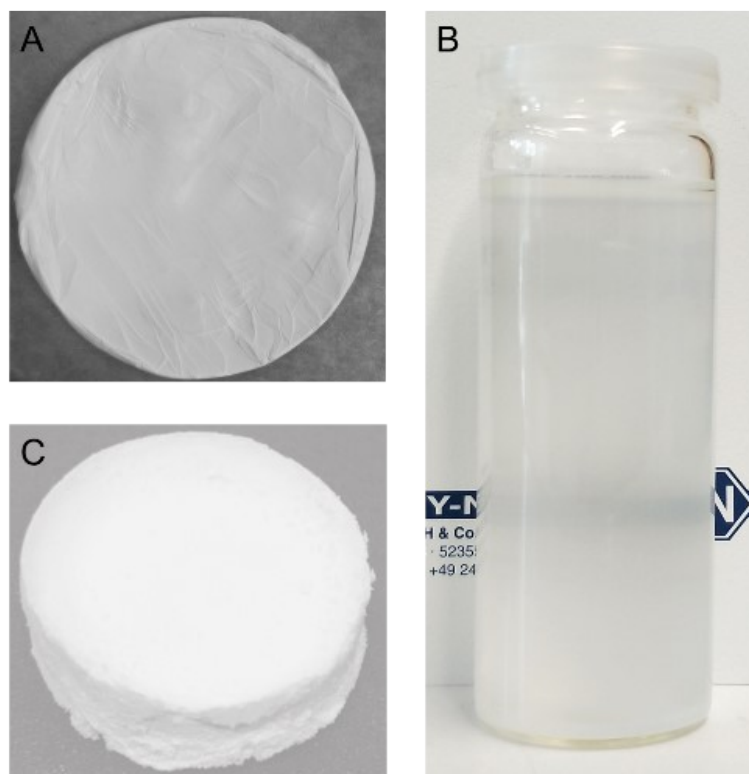
**Figure S13.** (A-E) PL spectra of PVEC/DMSO solution with different concentrations at different  $\lambda_{ex}$ . (F) Plots of PL emission peak and quantum yield versus concentration for PVEC/DMSO solutions ( $\lambda_{ex}=360$  nm). Inset: photographs of PVEC/DMSO solutions with different concentrations in daylight and under 365 nm UV light.



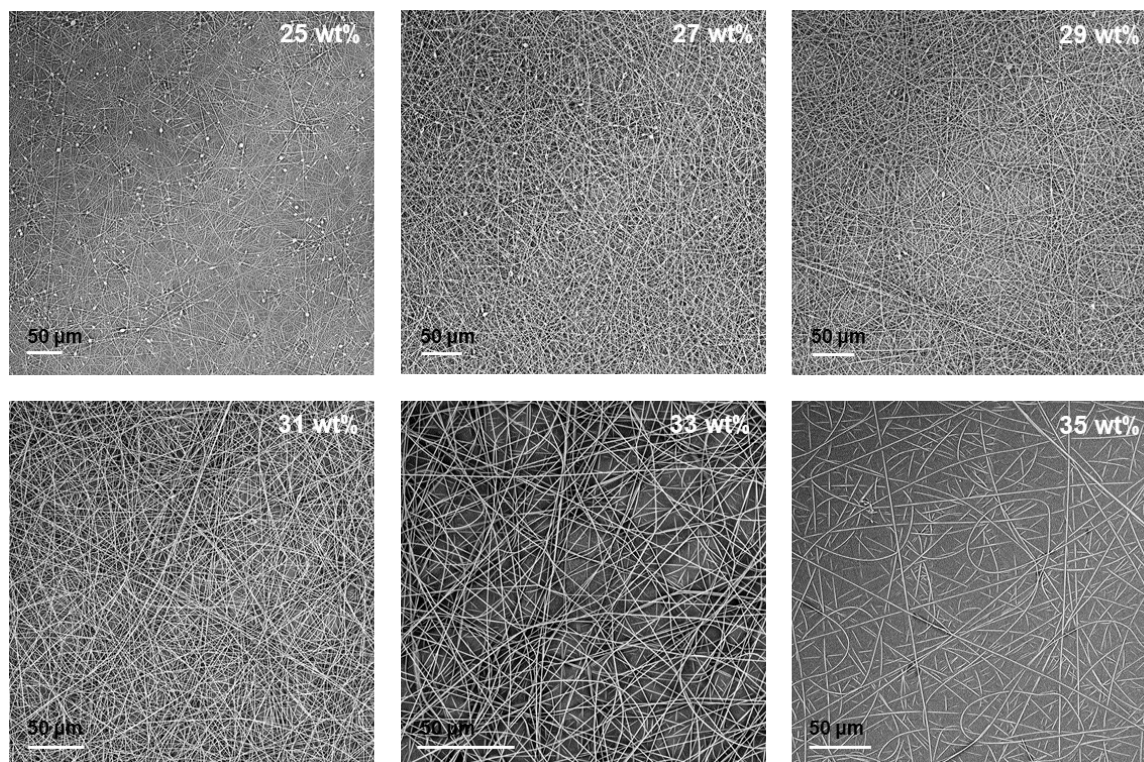
**Figure S14.** GPC curves in full range of PVC.



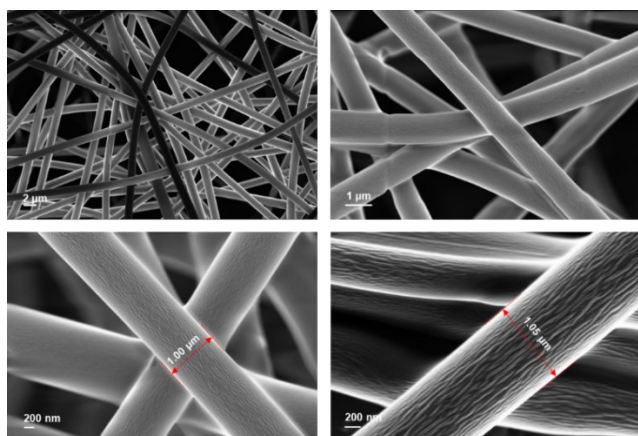
**Figure S15.** Theoretical calculations based on single polymer chains of PVEC with 10, 15, 20 constitutional units at (TD-DFT) B3LYP/6-31g(d) level. HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital.



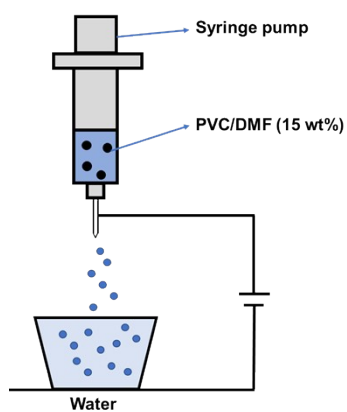
**Figure S16.** The digital photos of PVC fibers (A), microspheres (B) and sponges (C).



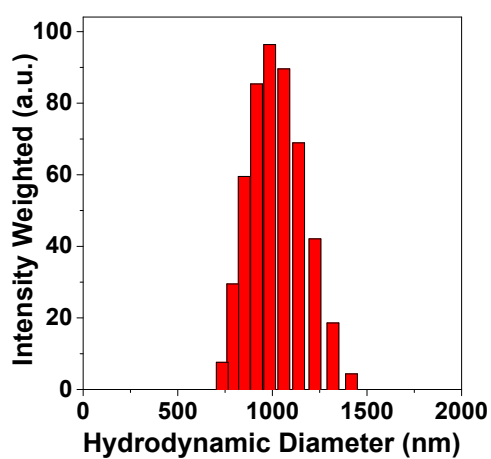
**Figure S17.** SEM photographs of PVC fibers electrospun from PVC/DMF solutions with different concentrations.



**Figure S18.** SEM photographs of PVC fibers electrospun from a 31 wt% PVC/DMF solution.



**Figure S19.** Schematic diagram of electrospay.



**Figure S20.** The hydrodynamic diameter of PVC microspheres in water measured by DLS at 25°C. (average diameter: 0.994 μm).

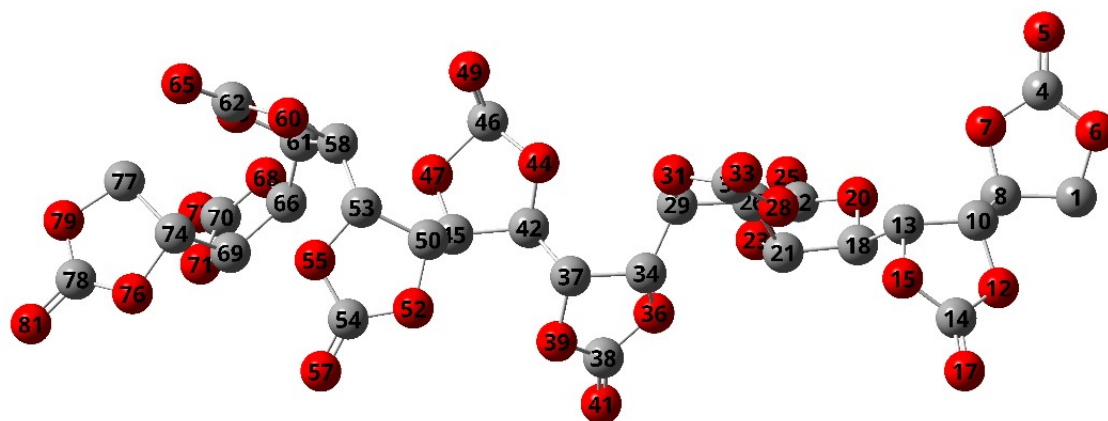
**Table S1.** Summary of elemental analysis of PVC and PVEC.

Sample	C (%)	H (%)	O (calculated, %)	Molecular formula
PVC-2.5KDa	37.48	24.97	37.55	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>
PVC-3.3KDa	37.50	25.05	37.45	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>
PVC-8.3KDa	37.54	25.01	37.45	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>
PVC-18.8KDa	37.49	24.94	37.57	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>
PVC-1436.7KDa	37.44	25.08	37.48	C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>
PVEC-8.5KDa	35.73	42.84	21.43	C <sub>5</sub> H <sub>6</sub> O <sub>3</sub>

**Table S2.** The calculated radiative ( $k_r$ ) and non-radiative ( $k_{nr}$ ) decay rates of PVC and PVEC in the solid state and DMSO solution, respectively.

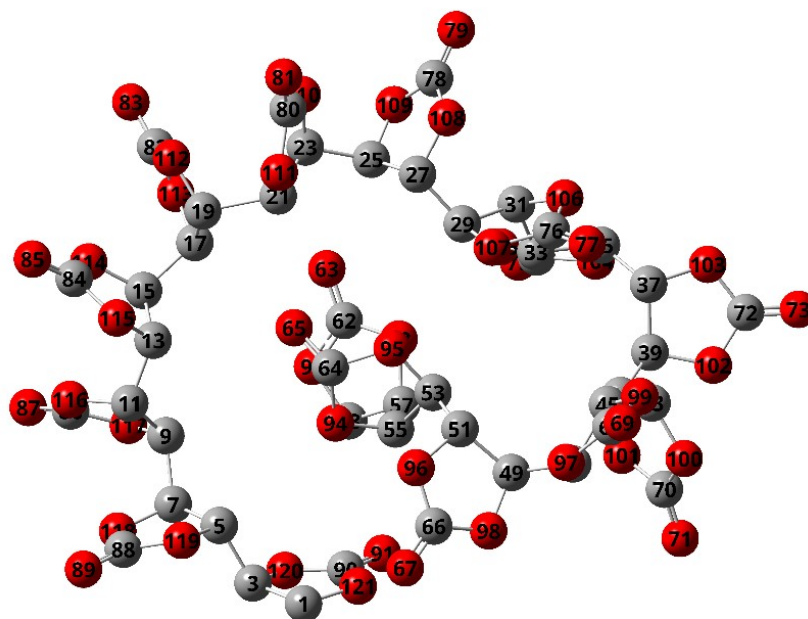
	$\Phi_F$	$\tau$ (ns)	$k_r$ (s <sup>-1</sup> ) <sup>a</sup>	$K_{nr}$ (s <sup>-1</sup> ) <sup>b</sup>
solid PVC	4.5%	4.3	$1.05 \times 10^7$	$2.22 \times 10^8$
PVC in DMSO	9.9%	3.6	$2.75 \times 10^7$	$2.50 \times 10^8$
solid PVEC	2.8%	5.4	$5.18 \times 10^6$	$1.80 \times 10^8$
PVEC in DMSO	11.7%	4.3	$2.72 \times 10^7$	$2.05 \times 10^8$

<sup>a</sup>  $k_r = \Phi_F/\tau$ , <sup>b</sup>  $k_{nr} = (1-\Phi_F)/\tau$ , where  $\Phi_F$  is the fluorescence quantum yield, and  $\tau$  is the fluorescence lifetime, respectively.

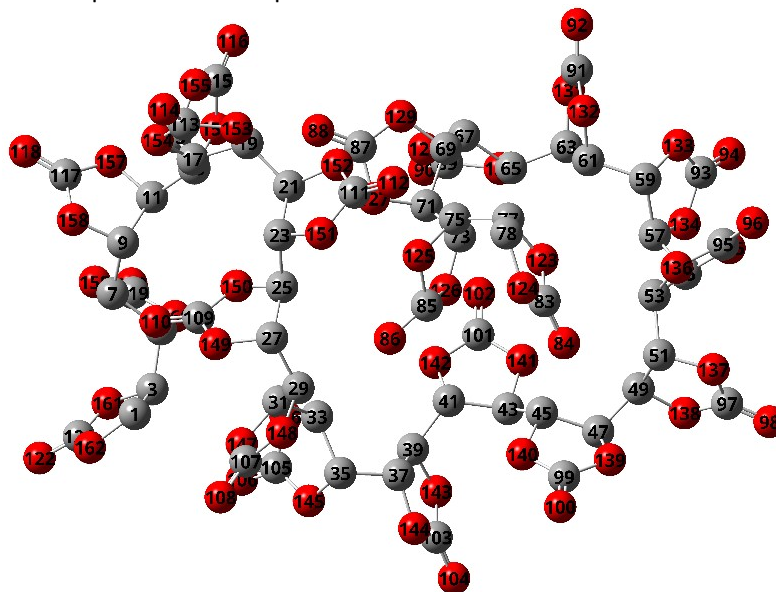
**Table S3.** Conformational parameters of optimized model of PVC-10.

O...O	distance (Å)	O...O	distance (Å)
O <sub>7</sub> ...O <sub>12</sub>	3.655	O <sub>47</sub> ...O <sub>52</sub>	3.601
O <sub>15</sub> ...O <sub>20</sub>	3.662	O <sub>55</sub> ...O <sub>60</sub>	2.989
O <sub>23</sub> ...O <sub>28</sub>	3.662	O <sub>63</sub> ...O <sub>68</sub>	2.889
O <sub>31</sub> ...O <sub>36</sub>	3.663	O <sub>71</sub> ...O <sub>76</sub>	2.795
O <sub>39</sub> ...O <sub>44</sub>	3.647		

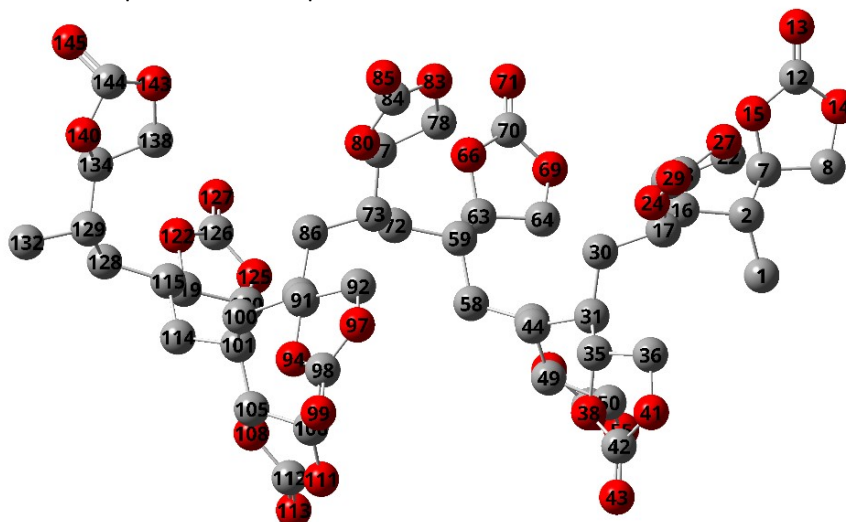
**Table S4.** Conformational parameters of optimized model of PVC-15.



O...O	distance (Å)	O...O	distance (Å)
O <sub>67</sub> ...O <sub>121</sub>	3.047	O <sub>103</sub> ...O <sub>104</sub>	3.007
O <sub>92</sub> ...O <sub>95</sub>	2.935	O <sub>109</sub> ...O <sub>110</sub>	2.751
O <sub>94</sub> ...O <sub>96</sub>	3.083	O <sub>111</sub> ...O <sub>112</sub>	2.937
O <sub>95</sub> ...O <sub>96</sub>	2.998	O <sub>113</sub> ...O <sub>114</sub>	2.767
O <sub>97</sub> ...O <sub>98</sub>	2.880	O <sub>115</sub> ...O <sub>116</sub>	2.887
O <sub>99</sub> ...O <sub>100</sub>	3.051	O <sub>117</sub> ...O <sub>118</sub>	2.952
O <sub>101</sub> ...O <sub>102</sub>	2.893		

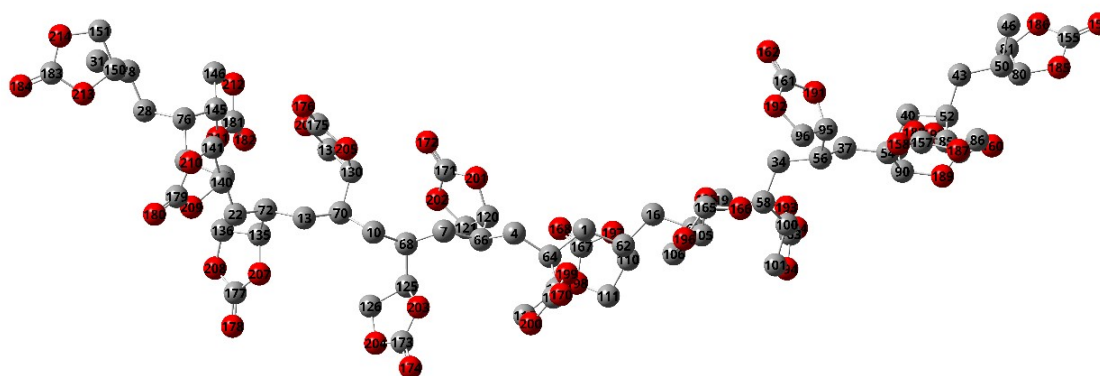
**Table S5.** Conformational parameters of optimized model of PVC-20.

O...O	distance (Å)	O...O	distance (Å)
O <sub>126</sub> ...O <sub>127</sub>	3.001	O <sub>146</sub> ...O <sub>147</sub>	2.867
O <sub>128</sub> ...O <sub>129</sub>	2.859	O <sub>148</sub> ...O <sub>149</sub>	2.832
O <sub>132</sub> ...O <sub>133</sub>	2.928	O <sub>152</sub> ...O <sub>153</sub>	2.866
O <sub>134</sub> ...O <sub>135</sub>	2.961	O <sub>154</sub> ...O <sub>155</sub>	3.086
O <sub>136</sub> ...O <sub>137</sub>	2.850	O <sub>156</sub> ...O <sub>157</sub>	2.829
O <sub>138</sub> ...O <sub>139</sub>	3.037	O <sub>158</sub> ...O <sub>159</sub>	2.940
O <sub>144</sub> ...O <sub>145</sub>	2.820	O <sub>160</sub> ...O <sub>161</sub>	2.835
O <sub>126</sub> ...O <sub>142</sub>	3.033	O <sub>88</sub> ...O <sub>156</sub>	2.950

**Table S6.** Conformational parameters of optimized model of PVEC-10.

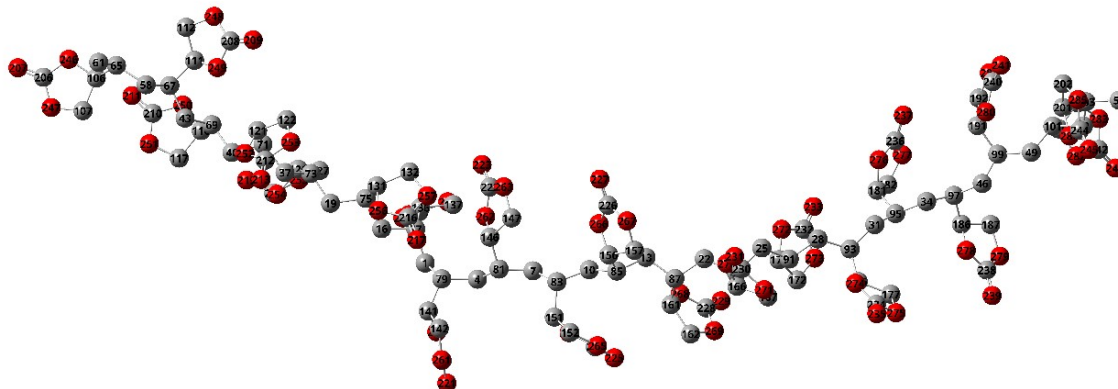
O...O	distance (Å)	O...O	distance (Å)
O <sub>15</sub> ...O <sub>27</sub>	5.043	O <sub>80</sub> ...O <sub>97</sub>	4.824
O <sub>24</sub> ...O <sub>41</sub>	4.896	O <sub>94</sub> ...O <sub>111</sub>	4.903
O <sub>38</sub> ...O <sub>55</sub>	4.889	O <sub>108</sub> ...O <sub>125</sub>	4.921
O <sub>52</sub> ...O <sub>69</sub>	4.817	O <sub>122</sub> ...O <sub>143</sub>	5.106
O <sub>66</sub> ...O <sub>83</sub>	4.873		

**Table S7.** Conformational parameters of optimized model of PVEC-15.



O...O	distance (Å)	O...O	distance (Å)
O <sub>182</sub> ...O <sub>206</sub>	3.397	O <sub>188</sub> ...O <sub>191</sub>	4.050
O <sub>200</sub> ...O <sub>203</sub>	4.709	O <sub>160</sub> ...O <sub>186</sub>	4.683
O <sub>168</sub> ...O <sub>201</sub>	4.216	O <sub>176</sub> ...O <sub>212</sub>	4.511
O <sub>196</sub> ...O <sub>199</sub>	4.654	O <sub>204</sub> ...O <sub>207</sub>	4.849
O <sub>192</sub> ...O <sub>195</sub>	4.167	O <sub>206</sub> ...O <sub>212</sub>	3.336

**Table S8.** Conformational parameters of optimized model of PVEC-20.





O...O	distance (Å)	O...O	distance (Å)
O <sub>249</sub> ...O <sub>250</sub>	4.580	O <sub>257</sub> ...O <sub>262</sub>	3.188
O <sub>247</sub> ...O <sub>251</sub>	4.843	O <sub>271</sub> ...O <sub>274</sub>	4.874
O <sub>250</sub> ...O <sub>254</sub>	4.801	O <sub>275</sub> ...O <sub>278</sub>	4.835
O <sub>257</sub> ...O <sub>263</sub>	3.353	O <sub>237</sub> ...O <sub>281</sub>	4.296

### Notes and references

- 1 N. D. Field and J. R. Schaefgen, *J. Polym. Sci.*, 1962, **58**, 533.
- 2 D. C. Webster, *Prog. Org. Coat.*, 2003, **47**, 77.