Thermoresponsive hybrid double-crosslinked networks using magnetic iron oxide nanoparticles as crossing points

Thomas Blin,a Antoine Niederberger,a Lazhar Benyahia,a Jérôme Fresnais,b Véronique Montembault* and Laurent Fontaine*a

a Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France
b Laboratoire de Physico-chimie des Electrolytes et Nanosystèmes Interfaciaux (PHENIX), UMR 8234 CNRS, Sorbonne Université, 75252 Paris Cedex 05, France
Synthesis of \([N\text{-methyl(dimethoxyphosphonyl)}\text{-}(3\text{-furanyl})\text{prop-2-yn-1-amine}~(2)\)

2 was synthesised in 1 step as follow (Scheme S1-B). \(N\text{-}(3\text{-furanyl)methylene})\text{prop-2-yn-1-amine}~1\) (1.372 g; 10 mmoles; 1 eq) and dimethyl phosphite (1.11 g; 10 mmoles; 1 eq) were placed in a 25 mL round-bottom flask equipped with a magnetic stirrer and a condenser. The reaction mixture was heated for 8 h at 60 °C. The \(\alpha\text{-aminophosphonate}~\)was purified by silica gel column chromatography eluted with acetonitrile (150 mL), then a gradient of ethyl acetate:acetonitrile, 80:20 (250 mL), and finally ethyl acetate (400 mL) to give the pure product as a yellow oil (55% yield).

\(^1\)H NMR (CDCl\(_3\)) (Fig. S2), \(\delta\) (ppm): 7.52 (m, 1H, O-\(\text{CH=CH}\)); 7.43 (m, 1H, O-\(\text{CH=CH}\)); 6.54 (t, \(J = 3.42~\text{Hz}\), 1H, O-\(\text{CH=CH}\)); 4.37 (d, \(J = 17.08~\text{Hz}\), \(\text{CH-P}\)); 3.77 (m, 6H, \(\text{CH}_3\)); 3.57-3.19 (m, 2H, \(\text{CH}_2\)); 2.26 (t, \(J = 3.93~\text{Hz}\), \(\text{C=CH}\)); 1.89 (s, NH).

\(^{13}\)C NMR (CDCl\(_3\)), \(\delta\) (ppm): 143.45; 141.85; 118.65; 110.25 (furan ring); 80.67 (C=CH); 72.50 (C=CH); 53.50 (CHP); 49.55 (d, \(J = 8.10~\text{Hz}\), \(\text{CH}_3\)); 35.70 (N-\(\text{CH}_2\)). \(^{31}\)P NMR (CDCl\(_3\)) (Fig. S3), \(\delta\) (ppm): 25.47.

Figures and Schemes

Scheme S1. Synthesis of \([N\text{-methyl(dimethoxyphosphonyl)}\text{-}(3\text{-furanyl})\text{prop-2-yn-1-amine}~(2)\) in two steps.
Figure S1. $^1$H NMR spectrum of $N$-(3-furanylmethylene)prop-2-yn-1-amine (1) in CDCl$_3$.

Figure S2. $^1$H NMR spectrum of $[N$-methyl(dimethoxyphosphonyl)-(3-furanyl)]prop-2-yn-1-amine (2) in CDCl$_3$ (*solvent residual peaks).
Figure S3. $^{31}$P NMR spectrum of \([N\text{-}\text{methyl(dimethoxyphosphoryl)}\text{-(3-furanyl)}]\text{prop-2-yn-1-amine (2)}\) in CDCl$_3$.

Figure S4 MALDI-TOF mass spectra of diazido-PEO (blue) and difuran-functionalized dimethylphosphonate PEO (red). The inset figure is an expanded region showing the constitutive unit of PEO; matrix: DCTB, NaTFA.

Scheme S2. Dealkylation of difuran-functionalized dimethylphosphonate-terminated PEO.
Figure S5. $^1$H NMR (left) and $^{31}$P NMR (right) spectra of difuran-functionalized dimethylphosphonate-terminated PEO (blue) and difuran-functionalized diphosphonic acid-terminated PEO (red).

Figure S6. TEM image of iron oxide nanoparticles.
Figure S7. DSC scanning of oxanorbornene-functionalized dimethylphosphonate-terminated PEO at 36 % w/w in DMSO.

Figure S8. Frequency dependence of the storage $G'$ and loss $G''$ moduli of 3D double-crosslinked network at 120 °C.