Supplementary information

Multicompartment nanocontainers from blends of terpolymers

Jean-François Gohy,[a]* Nathalie Lefèvre,[a] Cécile D'Haese,[a] Stephanie Hoeppener,[b] Ulrich S. Schubert,[b] Georges Kostov[c] and Bruno Améduri[c]

[a]*Institute of Condensed Matter and Nanosciences (IMCN), Bio- and Soft Matter (BSMA), Université catholique de Louvain (UCL), Place Pasteur 1, 1348 Louvain-la-Neuve, Belgium. Fax: ++3210479269, Tel: ++3210479269, E-mail : jean-francois.gohy@uclouvain.be*

[b]*Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstrasse 10, 07743 Jena, Germany.*

[c]*Ingénierie et Architecture Macromoléculaire, Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier (UMR 5253-CNRS), 8, rue de l'Ecole Normale, 34296 Montpellier Cedex 1, France.*

1. Characterization of poly(VDF-*ter*-HFP-*ter*-TFMA) terpolymers

Figure S1 shows the ^{19}F NMR spectrum of the dried poly(VDF-*ter*-HFP-*ter*-TFMA) terpolymer produced from an initial $[VDF]_0/[HFP]_0/[TFMA]_0$ molar ratio of 64/9/27 and in the presence of $IC_6F_{12}I$ as the chain transfer agent (CTA). This spectrum shows the presence of the characteristic peaks centered at −92.0 ppm assigned to the difluoromethylene groups located in the head-to-tail VDF chaining (i.e., normal VDF addition, $-CH_2-CF_2-CH_2-CF_2$) and the peaks at -113.2 and -115.8 ppm, assigned to defects of chaining (i.e. reversed $-CH_2-CF_2-CF_2-CH_2-$ and $-CH_2-CF_2-CF_2-CH_2-$ sequences), characteristic of the head-to-head addition of VDF. The signal centered at −94.9 ppm corresponds to the difluoromethylene group of the VDF unit adjacent to a TFMA unit[1] (regarded as alternated oligo(VDF-alt-MTFA) copolymeric units). A broad peak at −68.5 ppm is attributed to the fluorine atom in $-CF_3$ group of TFMA incorporated in the copolymer[2] while the signal of the monomer appears as a single signal at -65.7 ppm. The characteristic signals of HFP have been evidenced by the -71, -122, and -185 ppm, assigned to CF_3, CF_2 and CF groups, respectively. The signals of CTA are confirmed by the peaks centered at -122.1 and -124.2 ppm (central C_4F_8 group) and that adjacent to both this central group and methylene of VDF centered at -112.5 ppm. The characteristic end-groups of the copolymers terminated by a VDF unit appear at -40.0 ppm and -108.0 ppm which are assigned to $-CH_2CF_2I$ and $-CF_2CH_2I$, respectively. The presence of two different end-groups was explained by the special ability of VDF to undergo the addition of a macroradical onto the $CH_2=$ site (normal addition, major proportion: 95 mol-%, yielding head-to-tail addition), but also onto the $CF_2=$ one (reverse addition, minor proportion: 5 mol.%, yielding head-to-head addition). The absence of signal at -40.0 ppm shows that no chain was terminated by a $-CF_2I$ group. It is worth noting that the sum of $-CF_2I$ and $-CH_2I$ (termination by a VDF unit) corresponds to total end-chains (Figure S1). This proves the absence of end-chain terminated by a TFMA unit ($-C(CF_3,CO_2H)-I$) and HFP-I.

Both the weak stability of the C-I bond and the steric hindrance due to both CF_3 and CO_2H groups may explain this hypothesis. Moreover, the absence of $-CF_2$-I or $-CF(CF_3)I$ end-groups arising from HFP (absence of signals centered at -60 and -145 ppm, respectively) evidences that the transfer does not occur onto the macroradical terminated by HFP.[3] In addition, the absence of $-CF_2I$ for high molecular weight material was observed. This result can also be explained by the difference of reactivity between $-CF_2I$ and $-CH_2I$ species, as noted in previous works on the ITP of VDF.[2-4] Thus, $-CF_2I$ species is more reactive than $-CH_2I$ which explains the accumulation of $-CH_2I$ in the course of the copolymerization. In conclusion, the suggested decreasing order of reactivity is as follows: $-CF(CF_3)$-I > $-CF_2$-I > $-CH_2$-I.

Analysis of the ^{19}F NMR spectra allow us to assess the $DP_{n,\ VDF}$ (i.e., the number of VDF units), that of HFP, $DP_{n,,\ HFP}$ and that of TFMA, $DP_{n,\ TFMA}$ (i.e., the number of TFMA units) in the copolymer, from equations 1-3.

$$DP_{n,\ VDF} = 3 \times (\int CF_2^{at\ -40.0\ ppm} + \int CF_2^{at\ -94.9\ ppm} + \int CF_2^{at\ -108.0\ ppm}) / ([(\int C_4F_8^{from\ -122.0\ to\ -124\ ppm} -$$
$$2\ x \int CF_3^{from\ -71.0}/3)]8) \tag{1}$$

$$DP_{n,\ TFMA} = (\int CF_3^{at\ -68.5\ ppm}/3) / ([(\int C_4F_8^{from\ -122.0\ to\ -124\ ppm} - 2\ x \int CF_3^{from\ -71.0}/3)] / 8) \tag{2}$$

$$DP_{n,\ HFP} = (\int CF_3^{from\ -71.0\ ppm}/3) / ([(\int C_4F_8^{from\ -122.0\ to\ -124\ ppm} - 2\ x \int CF_3^{from\ -71.0}/3)] / 8) \tag{3}$$

where $(\int CF_x^{at\ -i\ ppm}$ represents the integral of the signal centered at $-i$ ppm assigned to CF_x (x = 2 or 3).

For example, for P3 (Table 1), equations 1-3 indicate that 25 VDF, 0.5 HFP and 26.5 TFMA units have been inserted in the poly(VDF-*ter*-HFP-*ter*-TFMA) terpolymer and $M_n = 5,900$.
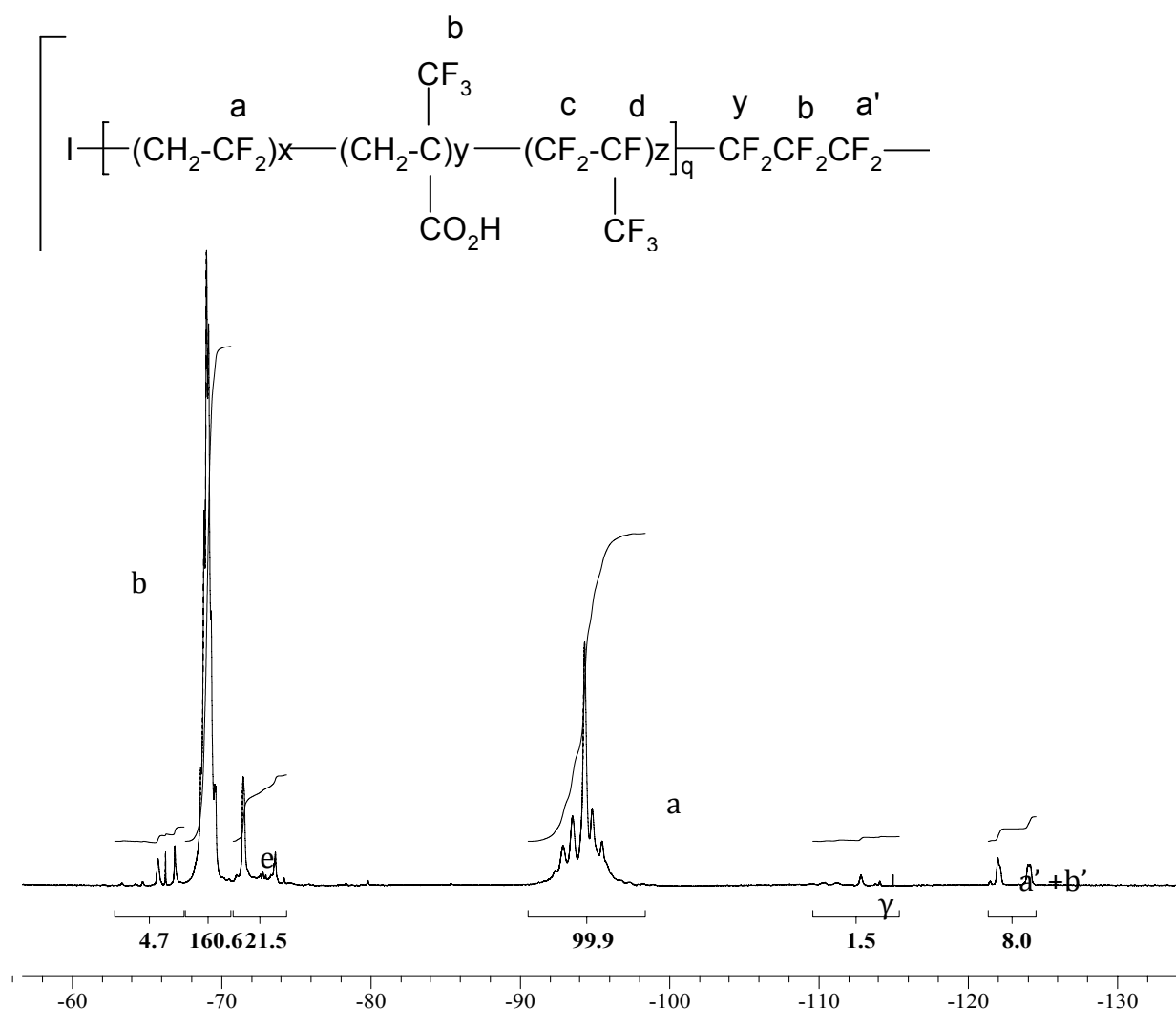
Figure S1. ^{19}F NMR spectrum (recorded in acetone d_6) of poly(VDF-*ter*-TFMA-*ter*-HFP) terpolymer, synthesized in emulsion (GKE9 in Table 1). Initial monomer molar ratio of VDF/TFMA/HFP=64/27/9; terpolymer composition of VDF/TFMA/HFP=45/49/6.

The ^{1}H NMR spectrum (Figure S2) confirms the terpolymerization of TFMA by the absence of signals at 6.5 and at 6.7 ppm assigned to the methylene group of the double bond (C$\underline{H}_2$=) of TFMA monomer. The spectrum also shows different multiplet and triplet centered in the 2.7-3.1 ppm range and 3.6 ppm which are attributed to -C$\underline{H}_2$- of VDF and TFMA and to –

$CF_2C\underline{H_2}$-I, respectively. The absence of the triplet of triplets centered at 6.3 ppm, assigned to $H$$CF_2CH_2$, shows that there is no observable transfer to water, to the monomers or to the copolymer itself.

The $-CF_2I$ amount in the poly(VDF-*ter*-HFP-*ter*-TFMA) terpolymer decreases with the number of VDF units inserted the polymer chain. This can be explained by the inversion of VDF during the polymerization and the difference of reactivity between $-CH_2I$ and $-CF_2I$ end-groups shown by their transfer constants (C_T = 7.7 and 0.3, respectively at 75 ^oC).[4] Indeed, a telechelic CTA gave a relatively more slow decrease of the $-CF_2I$ functionality versus the number of VDF units in the polymer. This is a surprising result, explained by the fact that, in the case of the telechelic CTA, both CF_2I sites generate one chain. The probability to have an inversion event increases with the number of VDF as described in a previous work.[4]

The targeted molar masses were determined from equation 4.

$$M_{n,\,targeted} = ([VDF]_0 \times M^{VDF} + [TFMA]_0 \times M^{TFMA} + [HFP]_0 \times MH^{HFP}) / ([CTA]_0 + M^{CTA})\ \textbf{(4)}$$

where [i], M^{TFMA}, M^{VDF}, M^{HFP}, M^{CTA} stand for the concentration of i reactant, the molar masses of TFMA (140 g.mol^{-1}), VDF (64 g.mol^{-1}), HFP (150 g.mol^{-1}), and of CTA (454 g.mol^{-1}), respectively.
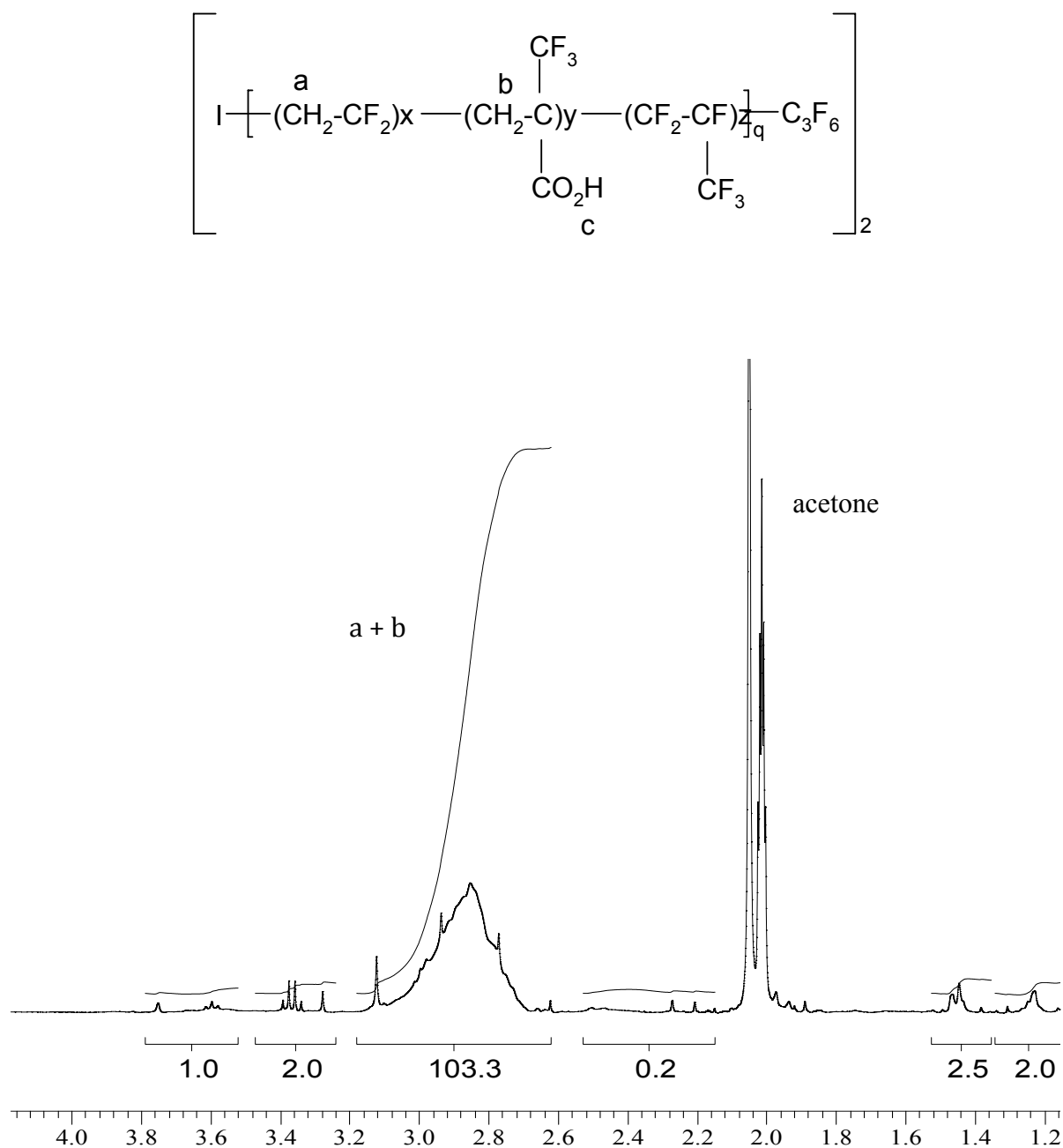
Figure S2. ^{1}H NMR spectrum (recorded in acetone d_6) of poly(VDF-*ter*-TFMA-*ter*-HFP) terpolymer, synthesized in emulsion (P2 in Table 1). Initial monomer molar ratio of VDF/TFMA = 64/27/9 mol %.; terpolymer composition of VDF/TFMA/HFP=45/49/6.

The determination of the composition of VDF, HFP and TFMA units in the copolymer was assessed from ^{19}F NMR analysis and equation 5 after purification.

Mol-% VDF in copolymer = $(\int CF_2^{\text{at} -39.0 \text{ ppm}} + \int CF_2^{\text{at} -94.9 \text{ ppm}}) / (\int CF_2^{\text{at} -39.0 \text{ ppm}} + \int CF_2^{\text{at} -94.9 \text{ ppm}}) + (2 \times CF_3^{\text{at} -68.5 \text{ ppm}}/3) + (2 \times CF_3^{\text{at} -71.0}/3)]$ **(5)**

where $\int CF_x^{\text{at} -i \text{ ppm}}$ represents the integral of the signal centered at $-i$ ppm assigned to CF_x (x = 2 or 3).

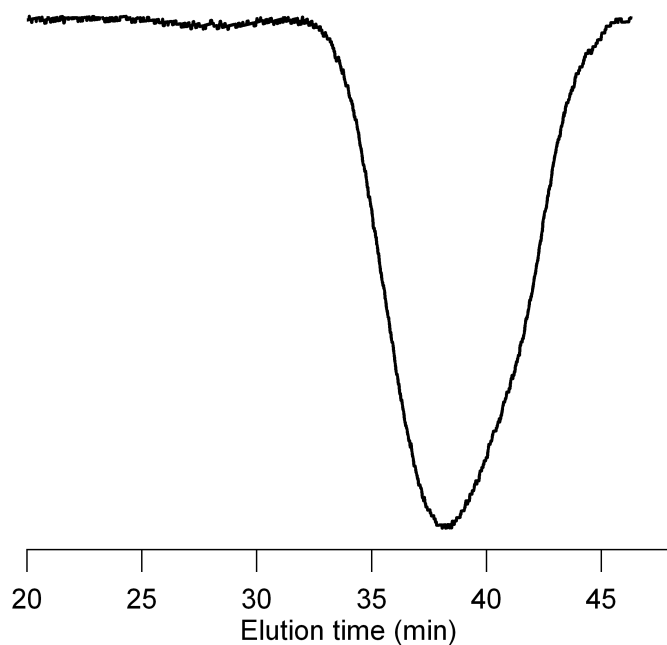The samples were also analyzed by SEC. A typical SEC curve is shown in Figure S3.

Figure S3. SEC trace of the P1 sample.
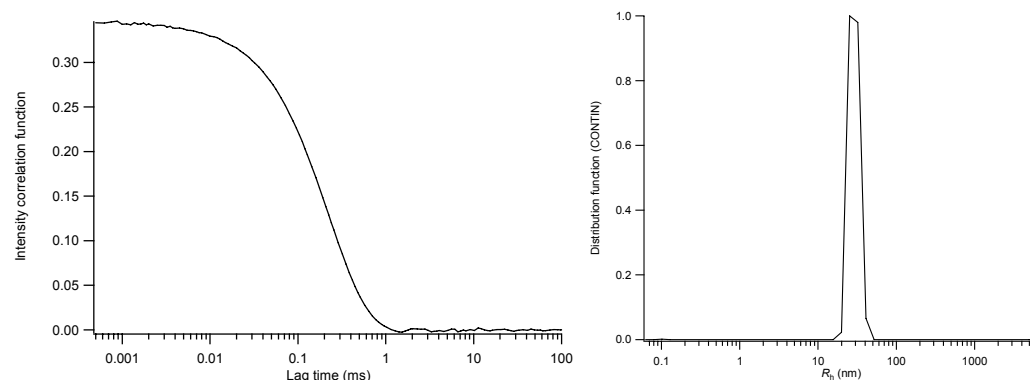
2. Additional DLS data

Figure S4. Experimental intensity correlation function (left) and CONTIN size distribution histogram (right) obtained for the P3/poly(S-b-2VP-b-EO) mixture in DMF at 1 g/L.
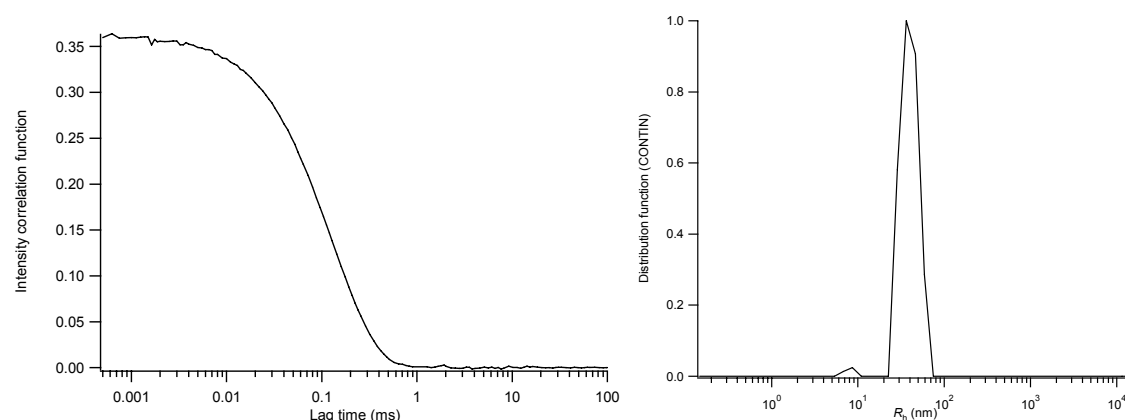

Figure S5. Experimental intensity correlation function (left) and CONTIN size distribution histogram (right) obtained for the GKE9/poly(S-b-2VP-b-EO) mixture in DMF at 1 g/L.

3. Encapsulation of a fluorophilic dye in the P1/poly(S-b-2VP-b-EO) mixture

The formation of VDF+HFP nanodomains in the P1/poly(S-b-2VP-b-EO) mixture has been deduced from the TEM picture of those nanocontainers shown in Figure 2. In order to further confirm the presence of such nanodomains, a fluorophilic dye has been encapsulated into the

VDF+HFP nanodomains. The same dye as the one previously synthesized and encapsulated into fluorodomains-containing micelles by Lodge and coworkers has been used.[5] This dye, namely 1-naphthyl perfluoroheptanyl ketone (NFH), should preferentially dissolved in the fluorinated nanodomains. A 5 mg/mL micellar solution of the P1/poly(S-b-2VP-b-EO) mixture was then mixed with an excess of NFH under stirring for one day. The UV-Vis adsorption spectrum of this solution was then measured (Figure S6) and revealed the characteristic absorption of NFH molecules encapsulated in fluorophilic domains at 298 nm, in perfect agreement with the data previously reported in ref. 5.
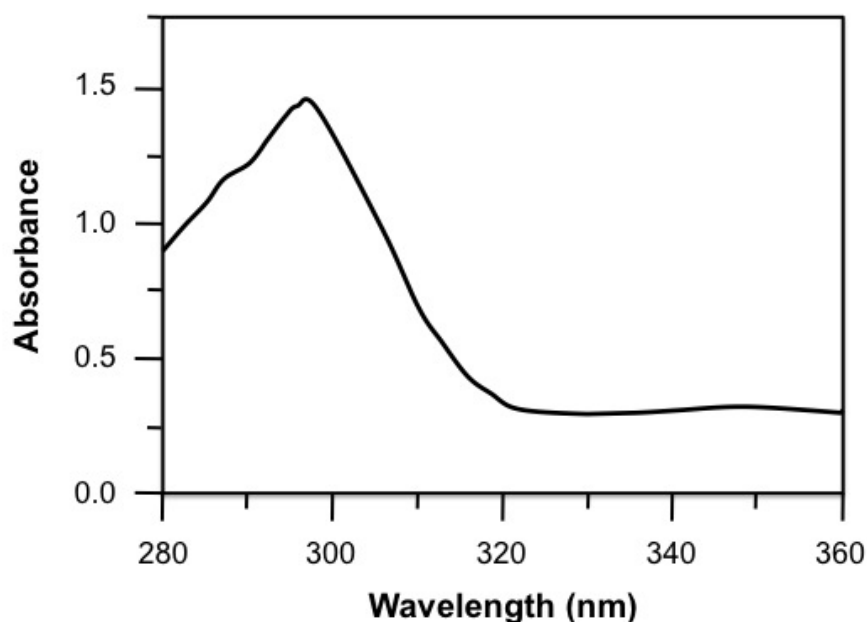

Figure S6. UV-Vis spectrum of the P1/poly(S-b-2VP-b-EO) mixture loaded with NFH.

4. References

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