CuAAC click chemistry: a versatile approach towards PVDF-based block copolymers†

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Alkyne/azide end terminated PVDF homopolymers were synthesized via free-radical polymerization using functional benzoyl peroxides as initiators. This approach allows the preparation of PVDF triblock copolymers with various functional blocks (poly(styrene, poly(N-isopropylacrylamide) and poly(tert-butyl acrylate)) and tunable crystallization behavior using copper(i)-catalyzed azide–alkyne cyclo-addition.

Electroactive polymers that change shape when triggered by an external electric field have attracted much interest over the past decades as highly promising candidates for various electronic devices. In particular, poly(vinylidene fluoride) (PVDF)-based ferroelectric polymers are widely studied because of their large polarization, high dielectric constant and low dielectric losses. Moreover, these polymers possess high thermal stability and desirable chemical inertness. The synthesis of block copolymers containing PVDF attracts a growing research attention as a promising strategy to introduce new functionalities into the polymer and to improve existing or to gain completely new properties. Furthermore, their ability to self-assemble into well-ordered structures in solution and in solid state can be used for the preparation of various nanostructured materials or advanced nanocomposites.

Although PVDF based block copolymers present highly valuable materials, their synthesis still remains a difficult task to achieve. The two main strategies to produce these materials are the synthesis of PVDF telomers followed by chain extension via ATRP12,14 and reversible deactivation radical polymerization (RDRP) techniques, such as iodine transfer polymerization (ITP)15 and reversible addition-fragmentation chain transfer (RAFT) polymerization using xanthate agents. The first method results in low molecular weight block copolymers with bimodal distribution. Additionally, ATRP leads to the formation of undesirable graft copolymers by the addition of propagating chains to PVDF double bonds caused by dehydroflourination. However, head-to-head coupling of VDF during RDRP prevents the preparation of high molecular weight polymers due to accumulation of less reactive \(-\text{CF}_2\text{-CH}_2-X\) (X = 1 or xanthate) chain ends during the reaction.22,23 In addition, Améduri’s group proved that \(-\text{CF}_2\text{-CH}_2-XA\) chain ends can start the polymerization of vinyl acetate, albeit at a slower rate.24 Again, both methods have faced new problems, mostly concerning the molecular weight of the PVDF that is too low for a successful film formation and practical applications. Moreover, in the second case, the RAFT polymerization is limited to only less activated monomers.

For these reasons, it would be of great interest to have alternative methods for synthesizing PVDF-based block copolymers. In 2007, Wang’s group reported the synthesis of PVDF and its copolymers with various well-defined end groups and relatively high end group fidelity (1.8–1.9) by using benzoyl peroxide(BPO)-based functional initiators. Our group further improved this strategy for the preparation of PVDF-based block copolymers. Owing to its robustness, modularity and high yields under relatively mild conditions, a copper(i)-catalyzed azide–alkyne cyclo-addition (CuAAC) was employed to prepare PLLA-b-PVDF-b-PLLA double-crystalline block copolymers. The similar approach is used by Vukicevic et al. and Guerre et al., where azide terminated PVDF, either made via ITP or RAFT, is applied for the preparation of block copolymers. The main idea of this widely used methodology is to obtain block copolymers by covalently bonding pre-synthesized ‘clickable’ building blocks.27 Even though exemplified by few specific block copolymers, CuAAC of telechelic PVDF and any other desirable block represents a promising strategy to synthesize PVDF-based block copolymers for advanced applications.

The current Communication reports the application and versatility of CuAAC in the preparation of PVDF-based block copolymers. The crucial step of this methodology is the syn-
thesis of telechelic azide and alkyne PVDF polymers which are used for further coupling. To achieve this task, we decided to use free radical polymerization initiated by functional BPOs, bearing in mind that the termination reaction in radical polymerization of fluorinated monomers occurs exclusively through the combination of radicals.28 Using the approach outlined in Scheme 1, the functional group of the benzoyl peroxide is present at both ends of the PVDF chains and can be used for subsequent reactions. In order to obtain azide terminated polymers, a chlorine functionalized initiator was used and after polymerization converted to azide, whereas an initiator having trimethylsilyl (TMS) protected ethynyl groups allowed successful preparation of alkyne terminated PVDF. Both BPO initiators were prepared from commercially available reagents via acylation of Li2O2 with functional benzoyl chloride, and further recrystallization. Polymers were obtained by solution polymerization of VDF in acetonitrile at 90 °C. Using acetonitrile as solvent is beneficial to minimize chain transfer to solvent, while the choice of the temperature was considered optimal taking in account molecular weight and yield. As exemplified in Fig. 1, the 1H-NMR spectrum of chlorine terminated PVDF reveals signals centered at 2.95 and 2.35 ppm, characteristic for head-to-tail and tail-to-tail sequences in the polymer backbone.28 The signals of phenyl protons at 8.07 and 7.65 ppm and methylene protons next to halogen atom at 4.80 ppm together with the appearance of the triplet centered at 4.68 ppm that corresponds to final methylene group bonded to the ester group from the initiator clearly show the incorporation of initiator fragments at the chain ends. Additionally, the small peaks at 6.29 and 1.79 ppm associated with –CH2–CF3H and –CF2–CH3 short branches that resulted from intramolecular branching reactions (backbiting) can also be observed.11,24,25,29 After stirring chlorine terminated PVDF with excess of sodium azide in DMF overnight and further purification, light yellow azide terminated PVDF is obtained. The complete shift of the signal corresponding to methylene protons linked to the halogen

![Scheme 1 Schematic representation of the synthesis of PVDF-based block copolymers using CuAAC click-coupling.](image_url)
atom from 4.80 to 4.60 ppm demonstrates the quantitative exchange of the end groups.

Following the same polymerization procedure as for the synthesis of chlorine terminated PVDF, polymers with terminal alkyn groups are prepared. The initiator used for the synthesis is functionalized with TMS protected ethynyl groups in order to avoid side reactions. The $^1$H-NMR spectrum of (TMS-alkyne)-PVDF (Fig. 1a and b), with no methylene protons, but with the existence of TMS-protecting group signal at 0.25 ppm, displays similar signals as in the case of chlorine terminated PVDF. The protecting group is cleaved by stirring the polymer with a slight excess of DBU in acetonitrile:water mixture for 2 h at 60 °C. The $^1$H-NMR spectrum of alkyn terminated PVDF provides clear evidence for the complete deprotection due to the disappearance of the TMS signal and the appearance of a new signal that belongs to the ethynyl proton at 4.51 ppm. During cleavage, the polymer color changes from light-yellow to light-brown. This suggests that a dehydrofluorination reaction takes place parallel to the removal of protecting groups. However, it has been observed before that with as little as 0.1% of dehydrofluorination, PVDF turns into a deep black polymer, as a result of the formation of conjugated C=C bonds within the polymer backbone. Moreover, the absence of a C=C bond signal at 6 ppm in the $^1$H-NMR spectrum is additional evidence that this unwanted phenomenon is present in a negligible amount. Both polymers, synthesized using different initiators, have similar polydispersity indices of around 1.5, while the molecular weight of the polymer synthesized using a chlorine containing initiator is higher. The main reason for small PDI values lies in the absence of disproportionation reactions together with an exhausting washing procedure that removes small molecular weight fractions. Additionally, we believe that the higher concentration of the alkyn containing initiator, caused by either better solubility and/or higher half-life compared to the initiator with the

<table>
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<tr>
<th>Product</th>
<th>$M_n,GPC$ [kg mol$^{-1}$]</th>
<th>PDI</th>
<th>$M_n,GPC$ [kg mol$^{-1}$]</th>
<th>PDI</th>
</tr>
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<tr>
<td>PVDF</td>
<td>14.4</td>
<td>1.49</td>
<td>11.6</td>
<td>1.60</td>
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<td>PS</td>
<td>8.2</td>
<td>1.20</td>
<td>9.8</td>
<td>1.18</td>
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<td>PtBA</td>
<td>12.2</td>
<td>1.22</td>
<td>12.0</td>
<td>1.15</td>
</tr>
<tr>
<td>PNIPAAm</td>
<td>11.7</td>
<td>1.27</td>
<td>11.3</td>
<td>1.22</td>
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<tr>
<td>PS-b-PVDF-b-PS</td>
<td>29.5$^a$</td>
<td>1.60</td>
<td>32.2$^a$</td>
<td>1.98</td>
</tr>
<tr>
<td>PtBA-b-PVDF-b-PtBA</td>
<td>34.7$^a$</td>
<td>1.37</td>
<td>29$^a$</td>
<td>1.62</td>
</tr>
<tr>
<td>PNIPAAm-b-PVDF-b-PtBA</td>
<td>36.0$^a$</td>
<td>1.54</td>
<td>31.4$^a$</td>
<td>1.75</td>
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$^a$ Molecular weight calculated from $M_n,GPC$ values of PVDF taking into account the ratio between the blocks calculated using $^1$H-NMR. The determination of molecular weight of block copolymers using GPC is not accurate bearing in mind that PVDF gives negative and the other polymers positive RI signals.

Fig. 2 $^1$H-NMR spectra in acetone-$d_6$ showing the successful preparation of PtBA-b-PVDF-b-PtBA block copolymers starting from (a) azide terminated PVDF and (b) alkyn terminated PVDF.
chlorine groups, is responsible for the difference in the molecular weights between polymers.

To evaluate the universality of this concept for block copolymer synthesis, three different polymers bearing complementary end groups, whether alkyne or azide, were synthesized. Polystyrene is chosen as a common polymer to test the alkyne/azide click reaction. On the other hand, poly(territ-butyl acrylate) (PtBA) is regularly used as a precursor for preparation of poly(acrylic acid), while poly(N-isopropylacrylamide) (PNIPAAm) is especially interesting due to its thermally responsive behavior in water. Both polymers, poly(acrylic acid) and PNIPAAm, are soluble in an aqueous environment and the preparation of block copolymers with PVDF represents a promising approach for the formation of pH and temperature responsive materials via self-assembly in solution.

All of the above-mentioned polymers are synthesized using RAFT, as it serves as a convenient and versatile technique with the possibility to obtain narrow molecular weight polymers with well-defined structures and end groups. The reactions are performed in the presence of RAFT agents, 2-(dodecylthio-carbonothioylthio)-2-methylpropionic acid propargyl (CTA-alkyne) or 3-azido-1-propanol ester (CTA-azide) at 70 °C. The use of the RAFT agents results in the formation of alkyne- or azide-terminated polymers that can be used in the CuAAC reaction with PVDF homopolymers. The molecular weight characteristics of the synthesized polymers are depicted in Table 1.

The last step to achieve PVDF-based triblock copolymers is coupling of already prepared end-functionalized polymers using copper(I)-catalyzed azide–alkyne cyclo-addition reaction. All reactions are performed in DMF at 60 °C in the presence of a copper(i) bromide-pentamethyldiethyltetraamine (PMDETA) complex. In order to gain full conversion of PVDF end groups and to avoid contamination of block copolymers with an unreacted PVDF homopolymer, a 1.3-fold excess of the other polymer is used. After 3 days, the reaction is stopped and the catalyst is removed by passing the polymer solution through a neutral aluminum oxide plug. Since one of the polymers had been used in excess, we washed the dried crude product with a selective solvent-good solvent for homopolymer (PS, PtBA and PNIPAAm) but a bad solvent for PVDF and the block copolymer. After a few centrifugation steps and solvent exchanges, the crude product is isolated and dried to give a pure block copolymer. The formation of the block copolymer and its purity is examined using 1H-NMR spectroscopy and gel permeation chromatography (GPC). The changes in the 1H-NMR spectra will only be explained for the reaction with PtBA, since the other block copolymers show similar results (Fig. S2–S5). After the reaction, if the azide terminated PVDF is used, the signals of the methylene protons next to the azide group of PVDF and next to the alkyne group of PtBA are both completely shifted from 4.60 and 4.71 ppm to 5.79 and 5.17 ppm, respectively, whereas a new signal for the triazole proton appears at 8.09 ppm (Fig. 2a). This all confirms the full conversion of PVDF into the triblock copolymer. Similar observations in the coupling reaction are made when alkyne terminated PVDF is used. A strong downfield shift of the signal assigned to the aromatic protons next to the alkyne group from 7.65 to 8.06 ppm, together with a total disappearance of the singlet corresponding to the terminal alkyne proton indicates a complete reaction (Fig. 2b).

Besides 1H-NMR spectroscopy, the successfulness of the click reaction is additionally proven by comparing GPC signals of homo- and block copolymers (Fig. 3). Independently of the end group combination and polymer type used in the reaction, the RI signal of block copolymer shows a shift to lower retention volumes compared to the homopolymer. Additionally, no signals related to unreacted homopolymers were observed demonstrating the preparation of pure block copolymers. Bearing in mind a small deviation from an ideal functionality of 2, an increase of the PDI values of block copolymers compared to homopolymers is expected. Under these conditions, a mixture of triblock and diblock copolymers is obtained, which gives rise to higher dispersity indices. The effect of polydispersity on the block copolymer self-assembly is still not fully explored, although recent studies showed a positive effect of polydispersity on the microphase separation. In the work of Mahanthappa and co-workers, the increased polydispersity of the middle block in ABA block copolymer drove the for-
formation of even richer phase behavior compared to the narrow-dispersed analogues. This suggests that block copolymers synthesized using the method reported in this communication, even though having a higher polydispersity, can be used as a platform to obtain piezoelectric nanostructures via microphase separation.

The ferroelectric properties of PVDF are a direct consequence of its crystalline structure, indicating the importance of block copolymer crystallization studies. Block copolymers can show high diversity of crystallization behavior, depending on their molecular characteristics. The crystallization nature of block copolymers upon cooling down from the melt, as well as the impact of the amorphous polymer structure on PVDF crystallization was studied using DSC. The polymers were heated to 200 °C, kept for 30 minutes and subsequently cooled down to room temperature. Fig. 4a depicts the crystallization exotherms of PVDF and its block copolymers indicating that crystallization temperature and degree of crystallinity are strongly influenced by the nature of the amorphous block. Such a variety of pathways is a direct consequence of two parameters: the interaction between blocks and the glass transition temperature of the amorphous block. In the case of PNIPAAm-b-PVDF-b-PNIPAAm, complete miscibility between PVDF and PNIPAAm above the melting point of PVDF is observed by using small angle X-ray scattering (SAXS) (Fig. 4b). The high miscibility of these two polymers is expected due to the hydrogen bond formation between the carbonyl group of PNIPAAm and the –CH2 groups of PVDF. PNIPAAm has a high Tg (Tg = 116 °C) that strongly affects the crystallization behavior of the block copolymer. The vitrification of the amorphous component occurs at a similar temperature as the crystallization of PVDF homopolymer, leading to a complete disruption of crystallization. As a consequence, strong undercooling and a substantial reduction of the crystallinity are observed.

Contrary to PNIPAAm-b-PVDF-b-PNIPAAm, due to unfavorable interactions between PtBA or PS and PVDF, the melt of these two polymers consists of PVDF spheres embedded inside a PS or PtBA matrix (Fig. 4b and c). The large contrast in their crystallization behavior lies in their different glass transition temperatures. The Tg value for PtBA (Tg = 43 °C) is not high enough to affect the crystallization process of PVDF. Therefore, PVDF crystallizes in the amorphous block, leading to a fully disrupted crystallization. The TEM images in Fig. 4c and d clearly show the confined crystallization of PVDF in the amorphous block, which is a direct consequence of the interaction between blocks and the glass transition temperature of the amorphous block.

Fig. 4 (a) DSC curves of PVDF and block copolymers obtained during cooling from the melt with 10 °C min⁻¹, (b) SAXS patterns of block copolymers recorded at 200 °C, (c) TEM image of PS-b-PVDF-b-PS after cooling from the melt indicating confined crystallization, (d) TEM image of PtBA-b-PVDF-b-PtBA after break-out crystallization.
Table 2  Crystallization of PVDF and its block copolymers

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<tr>
<th>Polymer</th>
<th>Tc (°C)</th>
<th>Xc (%)</th>
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<tr>
<td>PVDF</td>
<td>132</td>
<td>47</td>
</tr>
<tr>
<td>PS-b-PVDF-b-PS</td>
<td>53</td>
<td>21</td>
</tr>
<tr>
<td>PBA-b-PVDF-b-PBA</td>
<td>110</td>
<td>46</td>
</tr>
<tr>
<td>PNIPAAm-b-PVDF-b-PNIPAAm</td>
<td>66</td>
<td>4</td>
</tr>
</tbody>
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a Determined from DSC thermograms. b Calculated using the following equation: $X_c = (\Delta H_f / \Delta H_{100}) \times 100\%$. $\Delta H_f$ was determined from DSC thermograms while $f$ presents weight fraction of PVDF. $\Delta H_{100} = 104.5 \text{ J g}^{-1}$.

enough to prevent break-out crystallization of PVDF, and the formation of the lamellar structure consisting of PVDF crystals and amorphous part made of PVDF and PBA is inevitable (Fig. 4d). The degree of the crystallinity is equal to that of pure PVDF, while the reduction of crystallization temperature from 132 °C to 110 °C is attributed to the hindering effect of PBA (Table 2). On the contrary, after the solidification of the PS matrix, the crystallization of PVDF develops inside 3D confined spherical nanodomains (Fig. 4c). As a consequence, the crystallization temperature is reduced to only 53 °C, while the degree of crystallinity dropped two times compared to the homopolymer, still highly exceeding the values for PNIPAAm-b-PVDF-b-PNIPAAm. This example demonstrates the intriguing effect of microphase separation on crystallization which allows it to occur at lower temperatures, while preserving satisfactory crystallinity of the sample. It is evident that the abovementioned crystallization behavior is limited to the reported compositions only and that different ratios between the blocks together with the morphology formed in the melt can lead to completely different crystallization events. Nevertheless, this study is out of the scope of this communication and will be examined in future research.

In summary, telechelic PVDF polymers, bearing alkylene or azide end groups are synthesized using functional benzoyl peroxide initiators. These polymers are used for the preparation of different triblock copolymers with PS, PBA and PNIPAAm using a copper(I)-catalyzed azide–alkyne cyclo-addition. This synthetic route presents an alternative method to RAFT and ITP for the formation of well-defined block copolymers. The block copolymers show a rich crystallization behavior, highlighting the strong effect of the amorphous block’s molecular structure on crystal formation.

Conflicts of interest

There are no conflicts to declare.

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References