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Fullerenes Decorated with Poly(vinylidene fluoride)

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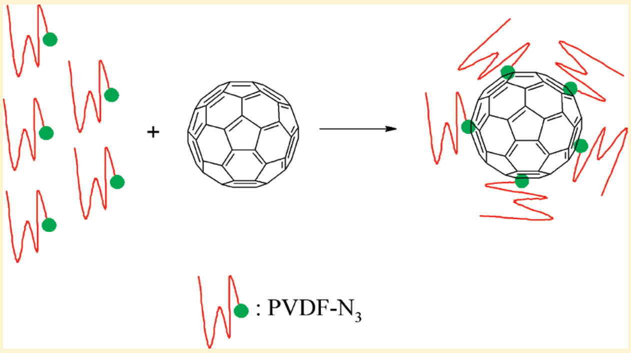
S *Supporting Information*

ABSTRACT: Fullerenes decorated with poly(vinylidene fluoride) (PVDF) were synthesized in a three-step procedure: Iodine transfer polymerization of vinylidene fluoride with $C_6F_{12}I_2$ as the chain transfer agent was carried out in supercritical carbon dioxide to synthesize iodine-terminated PVDF, which was subsequently transformed to azide-terminated polymer. Finally, azide-terminated PVDF chains were attached to a fullerene core under microwave irradiation at 160 °C in 1.5 h. The materials were characterized by NMR, FT-IR, UV/vis, GPC, elemental analysis, and DSC. On average, 4−5 PVDF chains are attached to one C_{60} moiety. FT-IR spectra and DSC measurements indicate that the polymer end groups strongly affect the crystallinity of the material. For PVDF with azide end groups and PVDF attached to fullerenes the fraction of the β polymorph is dominant while α polymorphs are almost absent.



INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is widely used for the fabrication of automotive materials, bearings, linings, vessels, and pipes because of its chemical, thermal, and mechanical stability. Moreover, PVDF has outstanding ferroelectrical,[1] pyroelectrical,[2] and piezoelectrical[3] properties. Therefore, it is employed for the preparation of infrared[4] and motion sensors,[5] supercapacitors,[6] actuators,[7,8] memory,[9] and energy harvesting devices.[10,11] On the other side, C_{60} is a very interesting compound for material engineering and may be used for preparation of ferromagnets,[12] superconductors,[13] organic photovoltaics,[14] and organic field effect transistors.[15] Hybrid materials consisting of PVDF and C_{60} are expected to combine the outstanding properties. However, the preparation of PVDF−fullerene composite materials is not easily feasible because of poor C_{60} processability. Thus, the aim of the present work is to covalently attach PVDF chains to fullerene molecules to enhance the compatibility of C_{60} and PVDF and to enable the preparation of PVDF-based hybrid materials.

The chemical modification of C_{60} molecules with polymers was reported in a number of studies. For example, fullerenes may be functionalized by macroradical trapping.[16,17] Another approach toward fullerene decoration is the nucleophilic addition of polystyrene from anionic polymerization.[18,19] Furthermore, since C_{60} molecules behave as 2π electron-deficient dienophiles, various cycloadditions can be employed for their modification.[20] Frequently, addition of azide-terminated polymers is used for fullerene decoration.[21−26] Wu et al. reported that C_{60} end-capped polystyrene and poly(methyl methacrylate) may be synthesized under microwave irradiation for times significantly shorter than in a conventional heating process.[27]

We report the synthesis of poly(vinylidene fluoride)−fullerene hybrid materials. PVDF with iodine end groups was synthesized in solution with supercritical CO_2 using the iodine transfer polymerization technique.[28−32] The iodine end groups were then transformed to azide end groups. Subsequently, the azide-terminated PVDF reacted with fullerene under microwave irradiation. The synthetic procedure is shown in Scheme 1.

EXPERIMENTAL SECTION

Materials. Fullerene (C_{60}, Iolitec, 99.5%), vinylidene fluoride (VDF, Dyneon, 99.5%), carbon dioxide (CO_2, Air Liquide, 99.8%), di-*tert*-butyl peroxide (DTBP, Merck, ≥98%), 1,6-diiodoperfluorohexane ($IC_6F_{12}I$, Alfa Aesar, 97%), *N*,*N*-dimethylacetamide (DMAc, Merck, 99%), sodium azide (NaN_3, Sigma-Aldrich, ≥99.5%), 1,2-dichlorobenzene (ODCB, Merck, ≥98%), lithium bromide (LiBr, Riedel-de Haën, 99%), acetone-d_6 (Deutero, 99.8%), acetone (VWR, 99%), potassium bromide (KBr, Fluka, spectranal), and diethyl ether (Roth, 99%) were used without further purification. For safe handling of sodium azide follow the material safety data sheet.

Synthesis of Poly(vinylidene fluoride) with Iodine End Groups (I−PVDF−I). Iodine transfer polymerization in solution with supercritical CO_2 was performed to synthesize I−PVDF−I. $IC_6F_{12}I$ was employed as the chain transfer agent and DTBP as the initiator. The reaction was carried out at 120 °C and an initial pressure of 1500 bar. The concentrations of $IC_6F_{12}I$, DTBP, and VDF were 0.14, 0.09, and 3.30 mol L^{-1}, respectively. The CO_2 content in the reaction mixture was

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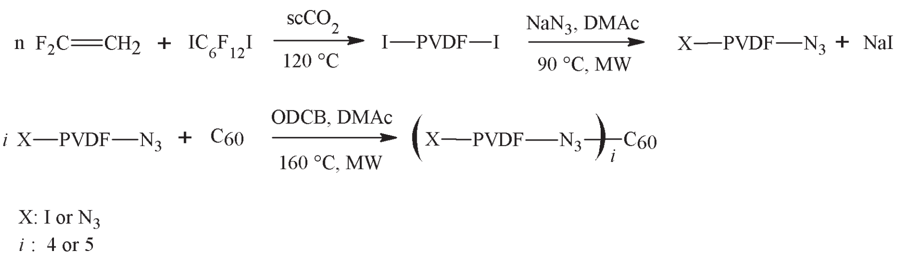
Scheme 1. Synthetic Strategy for the Functionalization of Fullerenes with PVDF[a]



[a] MW = microwave irradiation, ODCB = 1,2-dichlorobenzene, and DMAc = *N,N* dimethylacetamide.

73 wt %. The VDF conversion determined by in-line FT-NIR spectroscopy was 99%. Details on the experimental setup and the polymerization procedure are given elsewhere.[33]

Synthesis of Poly(vinylidene fluoride) with Azide End Groups. I−PVDF−I (480 mg, M_n = 1400 g mol^{-1}, 0.34 mmol), NaN_3 (170 mg, 2.62 mmol), and DMAc (7.0 mL) were stirred in a tube at 90 °C for 20 min under microwave irradiation. The maximum microwave power was 200 W. After the reaction, the mixture was poured into 100 mL of aqueous NaCl (0.5 mol L^{-1}) solution and left in a refrigerator overnight. Then, the precipitated polymer was separated from water and washed with deionized water three times to remove NaI and unreacted NaN_3. Finally, the polymer was washed with diethyl ether. The light brown product was dried in high vacuum and stored in a refrigerator at 2 °C. The yield was around 62%.

Synthesis of PVDF-Decorated Fullerene. In a flask C_{60} (200 mg, 0.28 mmol) was dissolved in ODCB (40 mL). In the second flask azide-terminated PVDF (200 mg, M_n = 1400 g mol^{-1}, 0.14 mmol) was dissolved in DMAc (10 mL). Then, the contents of both flasks were mixed, and a dark purple solution was obtained. The reaction mixture was stirred isothermally at 160 °C and ambient pressure for 90 min under microwave irradiation. The maximum microwave power was 100 W. The color of the reaction mixture changed from dark purple to dark brown. The solvents were removed using a rotary evaporator, and a dry residue was obtained. To separate PVDF decorated fullerene from the nonreacted fullerene acetone was employed, because low molecular weight PVDF and PVDF decorated fullerene are soluble in acetone, whereas pristine C_{60} molecules are insoluble in acetone. Then, the mixture was filtered in light vacuum. The solvent was evaporated from the liquid phase under reduced pressure. The solid residue obtained after solvent evaporation was dissolved in acetone and filtered, and the solvent was evaporated two more times. The final product was dried under high vacuum and stored at 2 °C. The yield was 65%.

Characterization. *Nuclear Magnetic Resonance Spectroscopy (NMR).* All NMR spectra were recorded on a Bruker 300 MHz spectrometer. Acetone-d_6 was used as solvent, and measurements were performed at room temperature.

Fourier Transform Infrared Spectroscopy (FT-IR). A Bruker Vertex 70 spectrometer equipped with a globar source and a DTGS detector was used for measuring Fourier transform infrared spectra with a resolution of 2 cm^{-1}. Samples were analyzed as pellets with KBr.

Ultraviolet−Visible Spectroscopy (UV−vis). UV−vis measurements were performed using a Perkin-Elmer Lambda 750 UV/vis spectrometer at room temperature from 250 to 600 nm. DMAc was used as solvent.

Size-Exclusion Chromatography (SEC). Molecular weight distributions were obtained by size-exclusion chromatography at 45 °C. The SEC setup consists of an Agilent 1200 isocratic pump, an Agilent 1200 refractive index detector, and three GRAM columns (10 μm, 8 × 300 mm, pore sizes 100 and 1000 Å) from Polymer Standards Services (PSS). *N,N*-Dimethylacetamide containing 0.1% LiBr was used as eluent. The SEC setup was calibrated using low-dispersity polystyrene standards (PSS).

Elemental Analysis. The weight percentages of carbon, hydrogen, nitrogen, iodine, and fluorine were determined by elemental analysis at the Mikroanalytisches Laboratorium of the Faculty of Chemistry at the University of Vienna.

Differential Scanning Calorimetry (DSC). DSC measurements were performed under a N_2 atmosphere using a Mettler Toledo DSC Star[e] system. For every sample the following procedure was employed: (1) heating from 25 to 180 °C at a rate of 20 °C/min; (2) isothermal at 180 °C for 2 min; (3) cooling from 180 to −90 °C at rate of 10 °C/min; (4) isothermal at −90 °C for 2 min; (5) heating from −90 to 180 °C at rate of 10 °C/min. The five-cycle analysis procedure was applied to ensure that all samples have the same thermal history. The data obtained in the last heating cycle were used for data evaluation.

RESULTS AND DISCUSSION

Iodine-terminated PVDF was synthesized by ITP of VDF in supercritical CO_2 ($scCO_2$). ITP is a very powerful polymerization technique which allows for the synthesis of fluoropolymers with tailored molecular weights (MW) and low dispersities.[28−30] For example, it was reported that perfluorohexyl iodide ($C_6F_{13}I$) used as chain transfer agent in VDF polymerization in $scCO_2$ gives access to PVDF with dispersities between 1.2 and 1.5.[34] To obtain a better control over the polymerization process, it appeared rewarding to use 1,6-diiodoperfluorohexane ($IC_6F_{12}I$) containing two iodine atoms that may be employed in ITP.[31,32] Additionally, $IC_6F_{12}I$ allowed for the synthesis of polymer chains with two iodine end groups which should result in more efficient fullerene functionalization. The ^1H NMR spectrum of iodine-terminated polymer (Supporting Information Figure S1) shows the following characteristic peaks (acetone-d_6, δ, ppm): 3.87 ($-\mathrm{CF_2}-\mathrm{C}H_2-\mathrm{I}$), 3.62 ($-\mathrm{C}H_2-\mathrm{CF_2}-\mathrm{I}$), 3.25 ($-\mathrm{C_6F_{12}}-\mathrm{C}H_2-\mathrm{CF_2}-$), 2.95 ($-(\mathrm{C}H_2-\mathrm{CF_2})_n-$), 2.35 ($-\mathrm{CF_2}-\mathrm{C}H_2-\mathrm{C}H_2-\mathrm{CF_2}-$). Between 0.8 and 1.5 ppm very weak peaks originating from initiator-derived end groups are seen. The peaks assigned to the polymer backbone and to $-\mathrm{C_6F_{12}}-\mathrm{C}H_2-\mathrm{CF_2}-$ were used to estimate the chain length of the material.[35] In all experiments PVDF with a molar mass of 1400 g mol^{-1} (derived from ^1H NMR) and a dispersity of 1.2 (derived from SEC) was employed.

PVDF with azide end groups was obtained from reactions of I−PVDF−I with NaN_3 in DMAc under microwave irradiation at constant temperature of 90 °C. The ^1H NMR spectrum of the product (Supporting Information Figure S1) exhibits the following peaks (acetone-d_6, δ, ppm): 3.87 ($-\mathrm{CF_2}-\mathrm{C}H_2-\mathrm{I}$), 3.25 ($-\mathrm{C_6F_{12}}-\mathrm{C}H_2-\mathrm{CF_2}-$), 2.95 ($-(\mathrm{C}H_2-\mathrm{CF_2})_n-$), 2.35 ($-\mathrm{CF_2}-\mathrm{C}H_2-\mathrm{C}H_2-\mathrm{CF_2}-$). The results from ^1H NMR and FT-IR spectra suggest that the iodine end group in $-\mathrm{CH_2}-\mathrm{CF_2}-\mathrm{I}$ reacts quantitatively with NaN_3, while iodine in $-\mathrm{CF_2}-\mathrm{CH_2}-\mathrm{I}$ is not reactive.[36] Since the conversion of I was not complete, different end groups were contained in the final

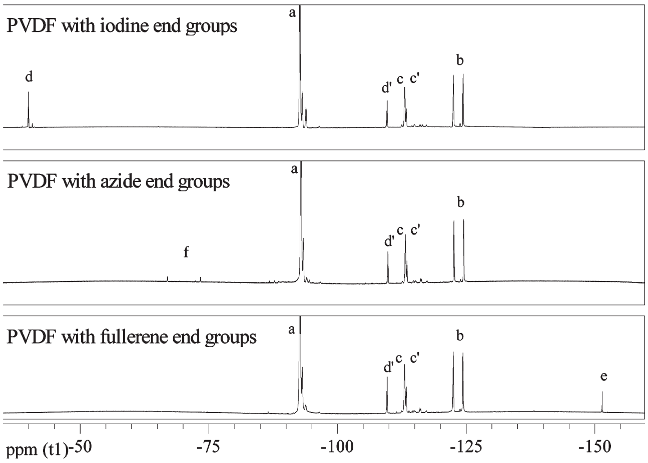


Figure 1. ^{19}F NMR spectra of PVDF with iodine and azide end groups and PVDF-decorated fullerenes. For peak assignments refer to Scheme 2.

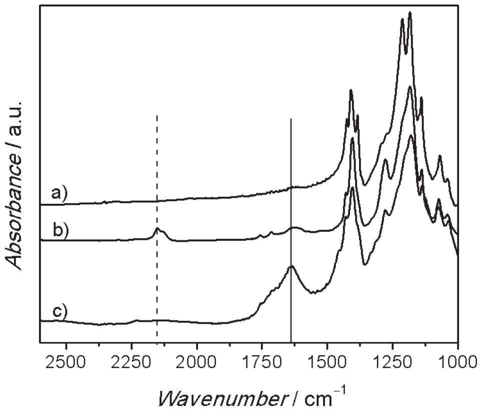
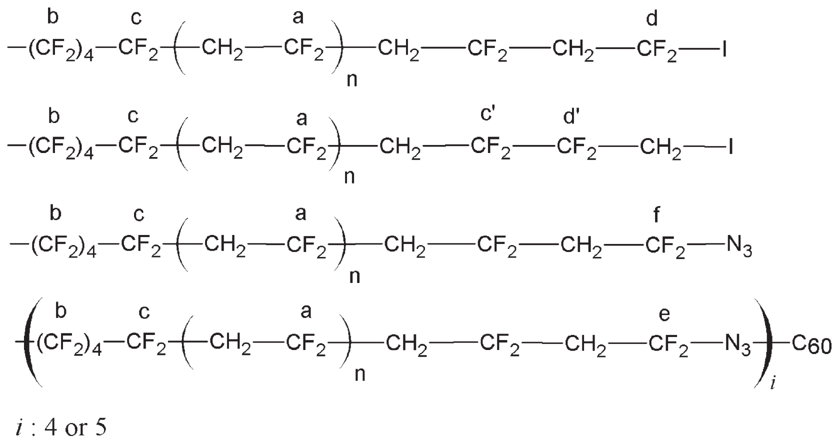


Figure 2. FT-IR spectra of (a) PVDF with iodine end groups, (b) PVDF with azide end groups, and (c) PVDF decorated C_{60}. The dashed vertical line indicates the absorbance due to the presence of azide end groups while the vertical solid line indicates the absorbance due to the C=C−N group.

Scheme 2. Assignments of Abbreviations Used for ^{19}F NMR Chemical Shifts in Figure *1* to Polymer Structure



material: I−PVDF−I, I−PVDF−N_3, N_3−PVDF−N_3. To facilitate the description in the remainder of the text, the polymer obtained from the reaction of I−PVDF−I and NaN_3 is referred to as azide-terminated PVDF.

The reaction between fullerene and azide-terminated polymer was carried out at 160 °C under microwave irradiation. Time required for the complete conversion of azide end groups was 90 min. To investigate the structure of the polymer with fullerene end groups, ^{1}H NMR and ^{19}F NMR spectra were recorded. The ^{1}H NMR spectrum of PVDF with C_{60} moieties was very similar to that of the original azide-terminated PVDF, and no signal corresponding to a proton in the neighborhood of the fullerene molecule was identified (Supporting Information Figure S1). Therefore, ^{19}F NMR spectra of I−PVDF−I, azide-terminated PVDF, and fullerene-terminated PVDF were recorded as shown in Figure 1. The peaks were assigned according to literature reports.[35−37] The assignment to the polymer structure is given in Scheme 2.

The peaks a, b, c, c′, and d′ are present in all PVDF samples. The peak d, assigned to $-CH_2-CF_2-I$, disappeared after the reaction between I−PVDF−I and NaN_3 while two new peaks, denoted as f, appeared. Peak f may be assigned to F atoms next to the azide group ($-CH_2-CF_2-N_3$). Since no information on ^{19}F NMR spectra of azide-terminated PVDF was available, the chain transfer agent $I-C_6F_{12}-I$ was treated with NaN_3. The characteristic peaks of CF_2-I at −64.6 ppm disappeared completely, and two new peaks at −66.9 and −68.4 were observed (Supporting Information Figure S2). These chemical shifts are rather close to the position of peaks f in Figure 1 and support the assignment. The presence of peak d′ in all samples suggests that iodine from the $-CF_2-CH_2-I$ end group does not react with NaN_3, which is in good agreement with the results obtained from ^{1}H NMR spectra. After the reaction between azide-terminated PVDF and fullerene, peak f disappeared and peak e, which is suggested to be assigned to the F atoms in the neighborhood of C_{60}, appeared. The ^{19}F NMR spectrum suggests that PVDF was successfully attached to fullerene molecules.

FT-IR spectra of the polymers with (a) iodine and (b) azide moieties and (c) the PVDF-decorated fullerenes are shown in Figure 2. The peak at around 2160 cm^{-1} (indicated by the dashed line in Figure 2) can be assigned to the azide moieties in the polymer.[38,39] PVDF containing only iodine end groups does not show any absorption at this wavenumber (a). After the reaction of azide-terminated PVDF chains with fullerenes, this peak disappeared, suggesting that complete consumption of azide moieties was achieved.[40] Additionally, the appearance of a new intensive peak at around 1640 cm^{-1} (solid vertical line in Figure 2) which can be assigned to the C=C−N group suggests that PVDF is chemically attached to the C_{60}.

The presence of fullerene in the polymer material was also examined using UV/vis spectroscopy. Figure 3 depicts UV/vis spectra of (a) azide-terminated PVDF, (b) pristine fullerene, and (c) fullerene decorated with PVDF molecules. The spectrum of C_{60} has a distinct absorption peak at around 330 nm in DMAc. PVDF with azide end groups shows little absorption while C_{60}-containing polymer has a pronounced shoulder around 330 nm. This finding is in agreement with literature reports on the synthesis of C_{60} end-capped polystyrene[21] and the synthesis of fullerene containing poly(alkyl methacrylates).[41] The result suggests that the reaction between PVDF and C_{60} has occurred.

In Figure 4, size exclusion chromatograms of (a) the starting polymer and of (b) fullerene functionalized with PVDF chains are shown. The measurements were carried out using an RI detector. Two significant differences in the SEC responses are noticeable. First, the starting polymer has a negative response due to the refractive index of PVDF being lower than that of the eluent. The elugram of the material after reaction with C_{60} has a major peak with positive RI response due to the increased refractive index of the material. This peak occurs at lower retention volumes than the initial material. Both findings suggest that a chemical bond between C_{60} and PVDF was established.

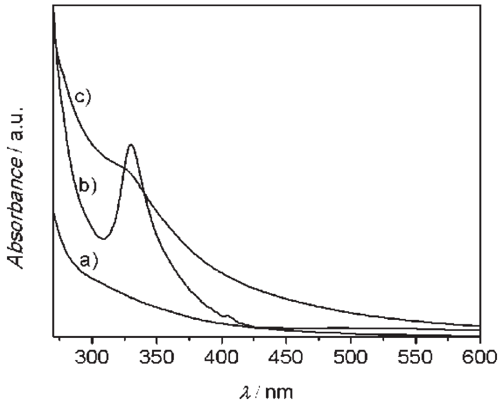


Figure 3. UV/vis spectra of (a) azide-terminated PVDF, (b) pristine C_{60}, and (c) fullerene decorated with PVDF.

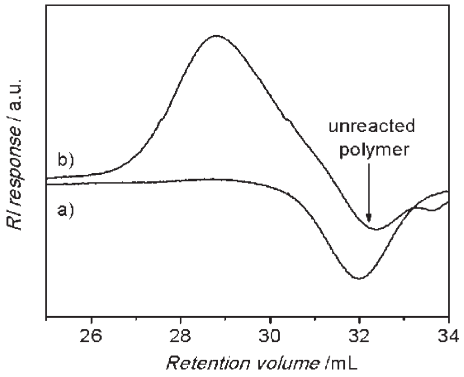


Figure 4. Size exclusion chromatograms of (a) starting PVDF and (b) C_{60} functionalized with PVDF.

Additionally, Figure 4b shows that there is a smaller second peak originating from unreacted polymer remaining in the synthesized material. As mentioned before, in the reaction between I−PVDF−I and NaN_3 the iodine atom in the $-CF_2-CH_2-I$ group is not reactive, and therefore not all I groups are changed into N_3 groups. This results in some PVDF molecules containing I groups at both chain ends which cannot react with fullerenes. The unreacted polymer has a lower molar mass than the starting polymer because the I atom in the $-CF_2-CH_2-I$ group is less reactive than that in the $-CH_2-CF_2-I$ group also during the iodine transfer polymerization.[31,35] Thus, the $-CF_2-CH_2-I$ end group occurs more often in chains with lower molar masses. Even though the SEC measurements showed that C_{60} functionalized with PVDF has a higher molar mass than the starting material, the elugrams do not allow for the determination of the average number of PVDF chains per fullerene molecule.

To determine the average number of polymer chains attached to a single fullerene, *i*, elemental analysis was performed. The results are shown in Table 1. With this data a molar mass of around 940 g mol^{-1} for the azide-terminated polymer is calculated. This value is somewhat lower than M_n derived from ^{1}H NMR spectra. The reason may be seen in the overlap of the peak at 3.25 ppm assigned to $(-C_6F_{12}-CH_2-CF_2-)$ with the peak at 2.95 ppm assigned to the polymer backbone $(-(CH_2-CF_2)_n-)$. As a consequence, the determination of the average number of monomer units per chain is affected. The fullerene content in the hybrid material was determined to be around 12.6 wt %. As shown by ^{1}H NMR, ^{19}F NMR, and SEC measurements the final PVDF−C_{60} material contains polymer chains which have unreactive I as end groups. This fraction has to be accounted for when the number of PVDF chains attached to one C_{60} molecule is estimated. For the fullerene functionalization reaction the number of PVDF molecules which have an inactive I group at both chain ends (I−PVDF−I) is very important. A higher number of such polymer chains is associated with less polymer molecules attached to C_{60}. Elemental analysis allows for the determination of the overall amount of unreactive I groups (CF_2-CH_2-I) in the final material, but it cannot provide information on the number of molecules that carries this group at one or at both chain ends. Therefore, two limiting cases are discussed. First, the worst case occurs when all inactive I groups are present in chains which have a CF_2-CH_2-I inactive group at both ends (I−PVDF−I). Then, the number of polymer molecules that cannot react with fullerene is maximal, and *i* is calculated to be 4. The second limiting case (the best case) occurs when there are no chains with unreactive I at both ends. Since all chains carry at least one reactive azide end groups, chains that are not able to react with C_{60} do not exist. In this case *i* is calculated to be 5. Thus, it may be concluded that the average number of PVDF chains per single C_{60} molecule is between 4 and 5. Another interesting conclusion which can be drawn from the results of the elemental analysis is that azide-terminated PVDF is attached to the C_{60} molecule by formation of triazoline

Table 1. Relative Amounts of C, H, N, F, and I in Azide-Terminated PVDF and Polymer-Decorated Fullerenes Obtained from Elemental Analysis (X Represents I or N_3 End Group)

sample	wt % C	wt % H	wt % N	wt % F	wt % I
X−PVDF−N_3	31.77	2.09	7.06	52.69	5.65
PVDF-decorated C_{60}	37.53	2.20	5.20	50.28	4.79

ring while nitrogen elimination does not occur. The relative amount of nitrogen in azide-terminated PVDF was 7.06 wt %, while after the reaction with C_{60} it decreased to 5.20 wt % due to the presence of fullerene in the polymer but not due to N_2 elimination (Table 1). If the nitrogen elimination had occurred, the relative amount of N in the final material would have been 2.1 wt %. Usually in the literature it is reported that at high temperatures alkyl azides are added to fullerenes by the formation of the intermediate triazole structure which is followed by the N_2 elimination.[24,42] The reason for the absence of the nitrogen elimination in the reaction presented here may be seen in the fact that the reaction was performed under MW irradiation, and thus the reaction time was much shorter, only 1.5 h, compared to the reaction times of 16 or 24 h reported in the literature.[22,24]

It is well-known that PVDF has five crystalline phases.[43,44] Different polymorphs in the polymer material may be distinguished by their FT-IR spectra.[45−47] The characteristic peaks of the α phase occur at 530, 615, 765, 795, 976, and 1178 cm^{-1}. The β phase is associated with absorptions at 510, 840, and 1275 cm^{-1}. Peaks at 512, 776, 812, 833, 840, and 1233 cm^{-1} are characteristic for the γ phase. It should be mentioned that the polar β phase is the most desirable polymorph from a technological point of view because it provides pyro-, ferro-, and piezoelectric properties. Figure 5 shows FT-IR spectra of iodine- and azide-terminated PVDF and of the PVDF-functionalized fullerenes. The characteristic α phase absorptions of PVDF at 765 and 795 cm^{-1} are clearly seen in Figure 5a while in Figure 5b, c these peaks can be hardly noticed. This suggests that in iodine-terminated PVDF the α phase is dominant while the β phase is of minor importance. The characteristic band at 840 cm^{-1}, which may be assigned to the β and γ phases, is present in Figure 5b,c, whereas the bands at 776, 812, 833, and 1233 cm^{-1} characteristic for the γ phase are absent. Thus, it may be concluded that the band at 840 cm^{-1} refers to the β phase. Additionally, the peak present at 1275 cm^{-1} in Figure 5b,c suggests that in azide-terminated and PVDF-functionalized C_{60} the β phase is dominant and the α phase occurs to a minor degree. The results indicate that by tuning polymer end groups the desired type of polymorphs in the PVDF material may be obtained. Thus, at least for the low-MW material polymer with dominant β polymorphs may be accessible by selecting a suitable synthetic route, and additional treatment of the material, e.g., like stretching or thermal annealing, may be avoided.

From the literature it is well-known that the various crystalline phases in PVDF are associated with different melting temperatures, T_m.[48] Thus, in addition, DSC measurements were performed to investigate the influence of fullerene on the thermal behavior and crystallinity of PVDF. Since the sample preparation was strongly different, expansion from solution with supercritical CO_2 in the case of I-terminated polymer vs isolation from a solution with organic solvents for the other two samples, and to avoid contributions from sample preparation, the second heating cycle was considered. Curves a and b in Figure 6, which correspond to iodine- and azide-terminated polymer, respectively, show two melting peaks. In PVDF with iodine end groups both α and β polymorphs are present. Since the α polymorph is dominant in I−PVDF−I (shown by FT-IR measurements), the prominent peak at around 123 °C in the DSC curve (Figure 6a) may be assigned to this phase. Then, the less intensive peak at around 94 °C corresponds to the β polymorph, which is the minor crystalline phase in the material. Although the FTIR spectra were recorded from the original material, this assignment is justified because the first and second DSC heating curves are not strongly different for I-terminated material. The same result was obtained for PVDF with a single I end group.[49] On the other hand, in azide-terminated PVDF FT-IR spectra suggest that the β phase is the dominant crystalline phase. Therefore, the peak at around 94 °C, corresponding to β phase, is more prominent than the one at around 123 °C, which corresponds to the α phase. However, in Figure 6c only one melting peak at around 100 °C is present. The FT-IR spectra suggest that this peak refers to the β phase. A second melting peak which may refer to the α crystalline phase is not observed. This finding may be explained as follows. The incorporation of C_{60} molecules at the end of the polymer chains suppressed the formation of the α phase and also increased T_m of the β crystalline phase. Chemical bonding of fullerenes to PVDF molecules results in reduced mobility of the polymer chains, and thus, T_m is increased. Previously, this reasoning was used to explain the significant enhancement of the glass transition temperature of polystyrene, if fullerenes are introduced into the polymer chain.[24] It is also interesting to note

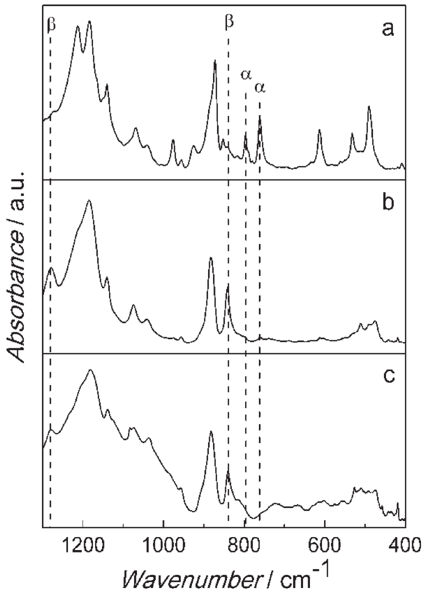


Figure 5. FT-IR spectra of PVDF with (a) iodine end groups, (b) azide end groups, and (c) PVDF-functionalized C_{60}.

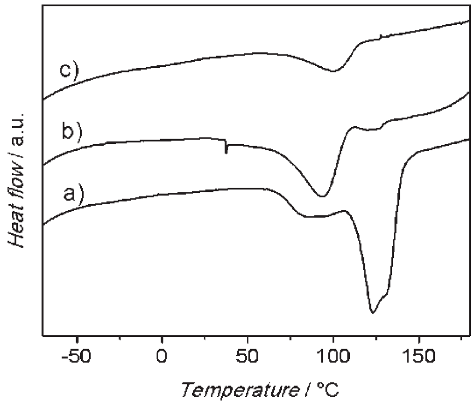


Figure 6. DSC curves of (a) I−PVDF−I, (b) azide-terminated PVDF, and (c) PVDF-decorated C_{60}.

that the overall crystallinity degree of the polymer material can be significantly changed by tuning the polymer end groups.[49] The overall degree of crystallinity, X, was calculated using the equation

$$X = \Delta H_m / \Delta H_c \times 100\% \tag{1}$$

The melting enthalpies of the sample, ΔH_m, were calculated by integration of the DSC curves shown in Figure 6, while the value for the enthalpy ΔH_c of 104.6 J g^{-1} for completely crystalline PVDF was adopted from the literature.[50] Although this calculation ignores that the melting enthalpies $\Delta H_m(\alpha)$ and $\Delta H_m(\beta)$ of the α and β polymorphs are different by around 10% ($\Delta H_m(\alpha)$ = 93.07 J g^{-1}and $\Delta H_m(\beta)$ = 103.4 g^{-1}),[51] the general findings are not affected by this approach. The degrees of crystallinity for the different polymers are X = 46% for PVDF with iodine moieties, X = 19% for the polymer with azide end groups, and X = 16% for PVDF-functionalized C_{60}. By substitution of the azide groups with C_{60}, the degree of crystallinity of the material is reduced, most probably because the bulky fullerene molecules hinder rearrangements of chain segments and the formation of crystalline phases within the polymer matrix. Previously, for a series of PVDF samples it was shown that material with C_6F_{13} and I end groups had an overall degree of crystallinity of more than 54%, whereas the crystallinity of PVDF with CCl_3 and Br end groups was ∼45% and 30% for PVDF with methyl end groups.[52] Thus, the rather high crystallinity of the I-terminated polymer may be assigned to the presence of perfluorinated hexyl groups in the polymer chain.

■ CONCLUSION

Starlike poly(vinylidene fluoride) with a fullerene core was synthesized by reaction of azide-terminated PVDF with C_{60} molecules at 160 °C under microwave irradiation in 90 min. The yield was 65%. The relative amount of fullerene in the final hybrid material was 12.6 wt %. The average number of polymer chains per single fullerene molecule was determined to be between 4 and 5. The overall crystallinity degree of the PVDF−fullerene hybrid material was around 16%. It is important to emphasize that in this hybrid material the dominant crystalline phase was the β phase, while there are no indication for the presence of the α phase.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR spectra of PVDF with different end groups as well as ^{19}F NMR spectra of $N_3-C_6F_{12}-N_3$ and $I-C_6F_{12}-I$. This material is available free of charge via the Internet at http://pubs.acs.org.

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