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On-Surface Growth Dynamics of Graphene

Nanoribbons:

The Role of Halogen Functionalization

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Abstract

On-surface synthesis is a powerful route toward the fabrication of specific graphene-like nanostructures confined in two dimensions. This strategy has been successfully applied to the growth of graphene nanoribbons of diverse width and edge morphology. Here, we investigate the mechanisms driving the growth of 9-atom wide armchair graphene nanoribbons by using scanning tunneling microscopy, fast X-ray photoelectron spectroscopy, and temperature-programmed desorption techniques. Particular attention is given to the role of halogen functionalization (Br or I) of the molecular precursors. We show that the use of iodine-containing monomers fosters the growth of longer graphene nanoribbons (average length of 45 nm) due to a larger separation of the polymerization and cyclodehydrogenation temperatures. Detailed insight into the growth process is obtained by analysis of kinetic curves extracted from the fast X-ray photoelectron spectroscopy data. Our study provides fundamental details of relevance to the production of future electronic devices, and highlights the importance of not only the rational design of molecular precursors but also the most suitable reaction pathways to achieve the desired final structures.

Keywords: graphene nanoribbons, on-surface synthesis, halogen substitution, reaction kinetics, fast X-ray photoelectron spectroscopy, scanning tunneling microscopy

Graphene, the most extensively studied sp^2 -bonded carbon material, has drawn great attention in the past decade because of its extraordinary electronic and optical properties.¹⁻³ However, the lack of an electronic band gap restricts its use in electronic devices which require switching capability with a high on/off ratio.^{4,5} On this basis, several approaches have been devised in order to establish a reliable band gap through structural modifications, namely the geometrical confinement of graphene sheets. Although confinement has been achieved *via* top-down approaches,^{6,7} a well-defined band gap is expected only for structures which exhibit atomically precise geometries. The bottom-up on-surface synthesis of quasi-one-dimensional (1D) graphene nanostructures, so-called graphene nanoribbons (GNRs),⁸ yields atomically precise width and edge structure, and is therefore considered as a breakthrough in quantum confinement of graphene. The most promising feature of GNRs is the width-dependent band gap. The width of an armchair GNR (AGNR) is expressed by N which represents the number of C-dimers across the ribbon. Density functional theory (DFT) calculations show that the band gap of AGNRs decreases with increasing width by the factor $1/(N+N_0)$, where N_0 is a constant,⁹ according to three different groups (families).¹⁰ Following the on-surface synthesis of the pioneering $N = 7$ AGNR (7-AGNR) on Au(111),⁸ several groups have reported various AGNRs such as 3-AGNR,^{11,12} 5-AGNR,^{13,14} 9-AGNR,¹⁵ 13-AGNR,¹⁶ 14-AGNR,¹⁷ 18-AGNR,¹⁸ 21-AGNR,¹⁷ as well as heteroatom-doped AGNRs.^{19,20}

Although the GNRs catalogue has expanded in recent years,²¹ the factors limiting their length have not been clearly addressed. An increased ribbon length is critical in view of employing these materials as active components in electronic devices. In order to fabricate a GNR-based field effect transistor (FET)^{6,22,23} the GNRs should efficiently bridge the source and drain

contacts, whose minimum distance (achieved by electron beam lithography) can be as small as about 20 nm.^{24,25} It is therefore crucial to shed light on the mechanisms driving the on-surface synthesis and thereby affecting the final length of GNRs.

The bottom-up synthesis of GNRs consists of sequential on-surface chemical reactions, namely dehalogenation, aryl-aryl coupling, halogen desorption and cyclodehydrogenation. The detailed sequence of all these steps has not been extensively investigated yet. Although low-temperature scanning tunneling microscopy (STM) provides morphological information at the atomic-scale, it has limited capability to monitor the surface during the course of a thermally activated chemical reaction. Therefore, a real-time inspection of the surface while the reactions take place is essential to identify all the intermediate steps and final products.

To this end, several studies made use of X-ray photoelectron spectroscopy (XPS) to monitor on-surface reactions by recording core level spectra as a function of temperature.²⁶ Nevertheless, the low resolution in temperature often inhibits a clear identification of the reaction pathways.^{27–}
³⁰ Here, we exploit fast-XPS to track the on-surface synthesis of 9-AGNRs and to unambiguously identify the sequence of reaction steps. 9-AGNRs have considerable potential to be exploited in FETs due to their band gap which is predicted to be 2.0 eV (for free-standing)^{9,10,15} and experimentally measured as 1.4 and 1.5 eV for metal-supported and metallic-alloy-supported ribbons, respectively.^{15,18} The electronic properties of Au(111)-supported 9-AGNRs based on the precursor molecule 3',6'-dibromo-1,1':2',1''-terphenyl (DBTP)¹⁵ (Scheme 1) have been experimentally investigated by combining scanning tunneling spectroscopy (STS) and angle-resolved photoelectron spectroscopy (ARPES).¹⁵ The in-depth characterization of the

9-AGNRs' growth steps and an improvement of the GNR length are thus appealing objectives in view of the realization of GNR-based electronic devices, and represent the core of the present work.

The average length of GNRs synthesized on surfaces is strongly influenced by the undesired termination of the sequential growth during polymerization. We have previously suggested that the origin of limited ribbon length is hydrogen passivation of the radical ends of the oligomers during the polymerization step.³¹ Suppressing (or limiting) this hydrogen passivation would thus allow the growth of longer polymers, and therefore longer GNRs. The hydrogen atoms involved in this process most likely originate from premature cyclodehydrogenation of the monomers and oligomers at particularly reactive surface sites. Consequently, lowering the polymerization temperature would be effective in decoupling these two reaction steps, and in turn, it would reduce the undesired termination of the polymer growth. Among the possible molecular functionalizations, we remain in the framework of aryl halides, which have demonstrated to be the most promising compounds to perform a well-controlled on-surface synthesis. We explore functionalization with iodine at the active sites of the precursor molecule (3',6'-diiodo-1,1':2',1''-terphenyl (DITP), Scheme 1) since it is known to detach from the phenyl at lower temperature than the previously used bromine (bond enthalpy with phenyl is 67 kcal·mol⁻¹ for I and 84 kcal·mol⁻¹ for Br³², and the energy barrier for dehalogenation on Au(111) has been calculated to be 0.71 eV for iodobenzene and 1.02 eV for bromobenzene).³³ If dehalogenation of the monomers is the rate-limiting step in the polymer formation, the use of DITP will allow the aryl-aryl coupling to occur at lower temperature than in the case of the DBTP.

In this paper, we thus compare two precursor monomers containing different halogens to analyze their impact on the growth of graphene nanoribbons, and describe the successful synthesis of 9-AGNRs with an average length of 45 nm on Au(111) using the iodinated precursor. We further provide fundamental insight into the reaction mechanisms by using a combined approach involving STM, fast-XPS, and temperature-programmed desorption (TPD) measurements.

Results and Discussion

The growth of 9-AGNRs has been studied by depositing DBTP or DITP (Scheme 1) onto Au(111) at room temperature (RT). Both molecules are designed to form 1D polymers *via* dehalogenative aryl-aryl coupling and subsequently GNRs upon cyclodehydrogenation, in a thermally activated two-step reaction. Figure 1 shows STM images of DITP on Au(111) at notable reaction steps (the topographic and electronic characterization of 9-AGNRs grown from the DBTP precursor has been previously reported).¹⁵

Scheme 1. Reaction scheme for the on-surface synthesis of 9-AGNRs. DBTP ($\text{X}=\text{Br}$) or DITP ($\text{X}=\text{I}$) have been used as precursors. The reaction is thermally activated on Au(111) and proceeds *via* two steps (with $T_1 < T_2$), involving aryl-aryl coupling (after dehalogenation) and cyclodehydrogenation.

After RT deposition of DITP on Au(111), two different phases of self-assembled molecules are observed (Figure 1a) as a function of coverage. At 0.1 monolayer (ML) phase 1 is obtained, while phase 2 appears at higher coverage (0.4 ML), becoming dominant and being characterized by islands with larger extension than for phase 1 (see Figure S1 in the Supporting Information). Hydrogen-halogen interactions are most likely stabilizing these phases which consist of intact molecules, as confirmed by the XPS measurements reported in Figure S2 in the Supporting Information. Annealing the surface at 160 °C induces the detachment of iodine atoms from the precursor molecules, followed by aryl-aryl coupling. At this stage, polymeric chains coexist with a network of iodine atoms adsorbed on the gold surface (Figure 1b). The structure of the obtained polymers (highlighted in Figure S3 in the Supporting Information) is the same as the one observed when using DBTP as precursor, and is thoroughly described elsewhere.¹⁵ It must be noted that some additional bright protrusions are visible at some parts of the polymer islands (Figure 1b and Figure S4 in the Supporting Information). We attribute these features to iodine atoms intercalated between the gold surface and the polymers. A similar behavior was also observed when using DBTP as precursor. The polymers are subsequently converted into GNRs *via* cyclodehydrogenation at 400 °C (Figure 1c). The defects visible in the STM images of the GNRs are attributed to the occasional dissociation of single phenyl groups in the last step of the reaction, as already reported for the growth from DBTP.¹⁵

Figure 1. STM images at subsequent reaction steps. a: Self-assembled phases of intact DITP after RT deposition on Au(111) ($V_b = -1.7$ V, $I_t = 10$ pA). b: Islands of polymers surrounded by a network of iodine atoms ($V_b = -1.5$ V, $I_t = 10$ pA). Bottom left and top right insets show magnified images of the iodine network and the polymer phase, respectively. c: Graphene nanoribbons obtained *via* cyclodehydrogenation ($V_b = -1.5$ V, $I_t = 5$ pA). The sample in c is obtained from a different preparation than that in a and b, starting with higher surface coverage of monomers. All images were acquired at 5 K.

To investigate the mechanisms leading to the formation of GNRs as a function of the different halogen functionalizations, we performed fast-XPS measurements, consisting of the acquisition of repeated XPS spectra (one spectrum every 5 s) during the annealing of the Au(111) from RT to 450 °C with constant heating rate of 0.2 °C $\cdot$ s $^{-1}$. Two energy levels are monitored at the same time, C 1s and Br 3d or I 4d, depending on the precursor structure. The resulting maps (Figure 2c-f), where each horizontal line corresponds to a XPS spectrum, allow for tracking of chemical shifts and provide a unique tool to monitor on-surface reactions.^{34,35} Figure 2b displays the total

areas of the halogen and carbon core levels extracted from the fast-XPS maps shown in Figure 2c-f, while Figure 2a reports separately obtained TPD measurements for these two systems.

According to the fast-XPS maps and the TPD data, the reaction pathways for DBTP and DITP share many similarities, and in the following we will stress the main differences that affect the final products. We first address the polymerization step of DITP. At about 80 °C the iodine atoms dissociate from the precursor and bind to the Au(111) surface, as demonstrated by the chemical shift observed for the I 4d level (with the I 4d_{5/2} peak shifting from 50.1 eV to 48.9 eV, Figure 2d). Within the same temperature range of 60 °C to 120 °C, the corresponding C 1s signal shifts from 284.1 eV to 283.7 eV, after which it remains unaltered up to about 300 °C (Figure 2f). STM investigation at 160 °C (Figure 1b) shows that 1D polymers are present at this temperature, and we can therefore attribute the observed C 1s shift to the polymerization step (*i.e.* aryl-aryl coupling). The same reactions take place when using DBTP as precursor, as seen by chemical shifts of Br 3d_{5/2} from 69.6 eV to 67.8 eV and of C 1s from 283.9 eV to 283.7 eV (Figure 2c, e). However, in this case the dehalogenation temperature is about 170 °C, due to the significantly higher dissociation energy of the Br-C bond compared to the I-C bond (as discussed in the introduction). While in some cases the diffusion of the surface-bound biradicals can be the rate-limiting step for the formation of polymers (as in the case of the growth of chevron-GNRs),³⁶ we observe that dehalogenation is the rate-limiting step in the two systems under investigation, since the aryl-aryl coupling readily occurs as soon as the halogens are detached from the monomers. In fact, the different dehalogenation temperatures for DITP and DBTP are reflected in distinct polymerization temperatures. This is of fundamental importance in terms of the polymer length, as will be shown in the following. We note that no signature of intermediate

organometallic phases has been observed by STM or XPS measurements. Furthermore, we note that at 120 °C polymers are formed for DITP, while we still observe intact monomers for DBTP (see Figure S5 in the Supporting Information). In the case of DBTP, a strong desorption of molecules occurs before the polymerization step, as revealed by a decrease in total area of the Br 3d and C 1s signals reported in Figure 2b. This prevents the growth of 9-AGNRs with significant surface coverage, as demonstrated by STM in Figure S6 in the Supporting Information. This desorption is not observed in the case of DITP because of its higher mass and lower temperature at which the polymerization takes place.

Further increase in temperature beyond 280 °C triggers the cyclodehydrogenation of the polymers into GNRs. From 280 °C to 430 °C the C 1s signals of the two systems (Figure 2e, f) present a shift of about 0.3 eV toward higher binding energy. This shift is associated with the formation of the extended π -electron system of ribbons, as proven by the STM image in Figure 1c and by the high-resolution (HR) XPS spectra acquired after each fast-XPS map (Figure S2 in the Supporting Information). In a similar temperature range (between 250 °C and 370 °C), the desorption of both halogens from the Au(111) surface takes place. This process, well visible in the fast-XPS maps in Figure 2c, d, can also be appreciated in the curves of the total areas reported in Figure 2b. TPD measurements in Figure 2a show that the desorption mostly occurs *via* hydrogenation of the halogens (HBr and HI masses have been detected), in agreement with a previous study.³⁷ Remarkably, the onset of halogen desorption is the same for Br and I. The fact that Br desorption is completed at lower temperature is simply due to a lower starting coverage, due to the monomer desorption described above. In fact, fast-XPS measurements demonstrate that, if the starting coverage of halogens is similar, identical desorption curves are obtained for

Br and I (Figure S7 in the Supporting Information). Due to their different masses, bromine and iodine are expected to desorb from the surface at different temperatures. However, we observe by fast-XPS the same desorption kinetics, witnessing that an additional mechanism is triggering halogen desorption from Au(111). We suggest that gold atoms of the surface might play a role in this process, as it is discussed below.

Figure 2. Real-time investigation of the on-surface reactions. a: TPD curves showing the desorption rates of HBr and HI as a function of increasing temperature (heating rate of $1\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$). b: Normalized total area of each horizontal profile of the fast-XPS maps. c-d: Fast-XPS maps of Br 3d, I 4d and C 1s recorded during the annealing (heating rate of $0.2\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$) of the Au(111) surface after deposition of the bromine precursor DBTP (c, e) or the iodine precursor DITP (d, f) at RT. Because of DBTP desorption upon annealing, the map in panel e has been normalized by the total area to highlight the energy shift. The original map is reported in Figure S8 in the Supporting Information.

Interestingly, we find that 9-AGNRs fabricated with the DITP precursor are systematically longer than the ones from DBTP. This observation is evidenced in Figure 3, where STM images of the GNRs obtained on Au(111) from the two precursors are shown. In the case of DBTP, the molecules have been deposited on the substrate held at 200 °C, to compensate the desorption observed during the annealing of the surface after RT deposition. Length histograms are used to compare the average length of 9-AGNRs obtained from DBTP and DITP, as previously reported for different GNRs.³⁰ Figure 3c reveals that the average 9-AGNR length is significantly increased from about 15 to 45 nm if the iodine precursor is used. We ascribe this improvement to the reduced probability for hydrogen passivation of the growing oligomers due to the lower polymerization temperature.³¹ The different sample preparation in the two cases - deposition on the substrate held at RT or 200 °C for DITP and DBTP, respectively - does not change the picture, since 9-AGNRs obtained from DBTP deposited on Au(111) at RT or at 200 °C show a similar length distribution (Figure S9 in the Supporting Information). Also the different coverages do not affect our interpretation, since similar coverage samples still reveal a significantly increased length for GNRs obtained from DITP (Figure S10).

Figure 3. STM images showing different length of 9-AGNRs obtained from DBTP (a, b) and DITP (d, e) (a: $V_b = -1.8$ V, $I_t = 30$ pA, b: $V_b = -1.5$ V, $I_t = 10$ pA, d: $V_b = -1.5$ V, $I_t = 50$ pA, e: $V_b = -1.5$ V, $I_t = 50$ pA). The histograms in c report the length distribution determined for the two systems using large-scale STM images, measuring about 800 ribbons in each case.

To shed further light on the sequence of reactions and mechanisms, we have extracted kinetic curves from the fast-XPS maps (as described in Figure S11 in the Supporting Information). We limit ourselves to the maps corresponding to DITP, because the strong desorption (leading to a reduction of the signal) and the smaller chemical shift for the C 1s signal render this analysis impossible in the case of DBTP.

The kinetic curves extracted from the I 4d and C 1s maps obtained with the DITP precursor are reported in Figure 4. Here, the dehalogenation and the aryl-aryl coupling (tracked at I 4d and C 1s levels) appear within the same temperature range and with similar sigmoidal line shape (see cyan and black curves from 40 °C to 130 °C). No significant shift in temperature is observed between the detachment of iodine from the precursor molecule and the polymerization, suggesting that the biradical species formed upon dehalogenation are sufficiently mobile to undergo immediate polymerization and that the dehalogenation is indeed the rate-limiting step for the aryl-aryl coupling. Contrarily, the reactions taking place at higher temperature (approximately between 270 °C and 430 °C) appear significantly different. They have the same onset temperature of 270 °C, but iodine desorption (cyan curve decreasing between 270 °C and 370 °C in Figure 4) is completed at 370 °C, while cyclodehydrogenation proceeds over a more extended temperature range (black curves between 270 °C and 430 °C).

To clarify the mechanism of iodine desorption, we also tracked the signal of pure iodine deposited on Au(111), that is in absence of any molecular species (red empty circles in Figure 4). The curve refers to the desorption of a sub-monolayer coverage of atomic iodine, comparable to that obtained starting from the DITP monomers (see Figure S12 in Supporting Information). This procedure allows to eliminate any possible effect of the molecular systems on the iodine desorption. Desorption of halogens from metal surfaces has been described in literature to occur along different pathways. For instance, desorption of AgI in the case of iodine on Ag,³⁸ and of Br, CrBr, and CrBr₂ in the case of bromine on Cr(100)³⁹ have been detected. Notably, no desorption of I₂ or Br₂ has ever been clearly reported. We observe a similar desorption onset (270 °C) for iodine cleaved from DITP and for pure iodine (cyan and red curves, respectively, in Figure 4). However, the two curves proceed with different kinetics. We tentatively suggest that

the iodine released from DITP molecules follows a desorption mechanism similar to the pure iodine at the initial stage (until 340 °C), which is most likely as AuI.³⁸ As soon as atomic hydrogen from the cyclodehydrogenation process becomes available on the surface, it enables an additional desorption channel for the iodine, as HI (detected by TPD, reported in Figure 2a), thus increasing the reaction rate and leading to a faster consumption of iodine (desorption is completed at 370 °C instead of 420 °C, measured for iodine alone). We ruled out any impact of the molecular hydrogen present in the residual gas, as demonstrated in Figure S13 in the Supporting Information.

The differences in the kinetics of iodine desorption and cyclodehydrogenation allow to separate the two processes by careful choice of annealing temperature and time. After deposition of DITP precursors on Au(111) at RT, we annealed the surface at 270 °C (onset of iodine desorption) for 20 minutes. The resulting surface is free of iodine but presents still the polymer chains, not yet converted into GNRs (Figure S14 in the Supporting Information). Such surface composition cannot be obtained *via* the standard heating ramp reported above, demonstrating the possibility of altering the growth pathways to obtain alternative phases.

Interestingly, the kinetic curves reported in Figure 4 exhibit different slopes. Monitoring kinetic profiles represents a valuable tool to qualitatively analyze reaction mechanisms. For instance, the curves related to the dehalogenation and polymerization processes can be fitted with second order kinetics with onset of 50 °C and activation energy of about 1.0 eV, assuming a pre-exponential factor (attempt frequency) of 10^{13} s^{-1} (Figure S16 in Supporting Information). This suggests a possible mechanism involving non-independent detachment of the two iodine atoms

within each monomer. Once the first iodine is detached, the energy barrier to remove the second could be lowered, leading to its immediate ejection and justifying a second order process. The polymerization has a similar kinetic curve, because it readily occurs after dehalogenation which is the rate-limiting step and determines the reaction order. The line shapes of the curves related to the iodine desorption and the cyclodehydrogenation cannot be fitted with simple kinetics. As we show in Figure S16 in the Supporting Information, combined equations and high reaction orders are needed to provide a good fit, but the mechanistic interpretation of these results is not trivial and will be object of further studies. Nevertheless, an activation energy of 1.8 – 2.0 eV for the cyclodehydrogenation step can be estimated from the fitting.

Figure 4. Kinetic curves extracted from the C 1s (black) and I 4d (cyan) fast-XPS maps of DITP. The maximum intensity of each signal is related to the corresponding surface coverage before the reaction and has been normalized to 1. The curves show that the transformation of the precursor into polymers and surface adsorbed iodine atoms takes place between 40 °C and 130 °C, while the desorption of iodine atoms and the cyclodehydrogenation transforming the polymers into GNRs occur at higher temperatures beyond 270 °C. The kinetic curve for the desorption of iodine alone (in absence of any molecular specie on the surface) is reported for comparison (red empty circles).

Conclusions

The on-surface synthesis of 9-AGNRs on Au(111) and the differences related to the nature of the halogen atoms used in the precursor molecules have been carefully investigated. We have shown by STM that the use of iodine-containing molecules leads to systematically longer graphene nanoribbons compared to those synthesized from the brominated compound. Fast-XPS measurements unveil the reason for this different growth, which is related to the lower dehalogenation temperature for DITP, reducing the cross-talk between the polymerization and cyclodehydrogenation steps and therefore limiting the passivation of growing chains by atomic hydrogen. Details in the mechanisms driving the synthesis of 9-AGNRs are provided by the kinetic curves extracted from the fast-XPS maps, showing the sequence of reactions occurring as a function of the temperature and their distinctive features. The rate-limiting step for the formation of polymers is the dehalogenation, which follows a second order kinetics, with an onset of 50 °C and an activation energy of 1.0 eV when using DITP as precursor. Iodine desorption starts at 270 °C and is completed at 410 °C for iodine alone, and at 370 °C if atomic hydrogen (arising from the cyclodehydrogenation) is available at the surface. The formation of ribbons starts at 280 °C and completes at 430 °C. The corresponding activation energy is in the range of 1.8 – 2.0 eV. The results reported in this work clarify some critical aspects concerning the growth of graphene-like nanostructures *via* dehalogenative polymerization and cyclodehydrogenation. We demonstrated that the nature of the halogen contained in the precursor molecules has a strong influence on the sequence of reactions, and consequently on the

final product. Such fundamental insight is useful for future studies aiming at the rational design of low dimensional carbon-based materials.

Methods

The preparation of 3',6'-dibromo-1,1':2',1''-terphenyl (DBTP) is reported elsewhere,¹⁵ while 3',6'-diiodo-1,1':2',1''-terphenyl (DITP) was synthesized according to the procedure reported in the Supporting Information. The high purity was confirmed by ¹H NMR analyses prior to the on-surface experiments. All the on-surface synthesis experiments were performed in ultrahigh vacuum (UHV) with base pressure better than 2×10^{-10} mbar. Au(111) (MaTeck GmbH) surface was cleaned by repeated cycles of Ar⁺ sputtering (1 keV) and annealing (470 °C). The precursor molecules were thermally evaporated on the clean surface from quartz crucibles heated at 55 °C (DBTP) and 95 °C (DITP), yielding a deposition rate of $0.5 \text{ Å} \cdot \text{min}^{-1}$. The deposition of pure iodine on the surface was performed dosing iodine gas on the clean Au(111) at RT *via* a leak valve with a partial pressure of 3×10^{-8} mbar for 45 s (exposure = 1.35 L). STM images were acquired with a low-temperature scanning tunneling microscope (Scienta Omicron) operated at 5 K in constant-current mode using a tungsten etched tip. All the bias voltages are referred to the sample (so that empty states are imaged at positive bias). X-ray photoelectron spectroscopy measurements were performed at the X03DA beamline (PEARL endstation)⁴⁰ at the SLS synchrotron radiation facility (Villigen, Switzerland), using linearly (and partially circularly

left/right) polarized radiation with photon energy of 425 eV. XPS spectra were obtained in normal emission geometry, using a hemispherical electron analyzer equipped with a multichannel plate (MCP) detector. HR-XPS spectra were recorded at RT in “swept” mode with 20 eV pass energy, while the fast-XPS measurement was performed during the heating of the sample (constant heating rate of $0.2\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$) using the “fixed” mode (snapshots of the Br 3d, I 4d and C 1s level) acquiring each spectrum for 5 s with 100 eV pass energy. The fast-XPS maps have a resolution of $3.5\text{ }^{\circ}\text{C}$ in temperature and 17 s in time. TPD experiments were performed using a quadrupole mass spectrometer (Pfeiffer QMA 200) to detect specific masses (in particular 80 for HBr and 128 for HI). A sample heating rate of $1\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$ was used in all TPD experiment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Includes additional experimental data (STM images showing DITP deposited on Au(111) at RT, details of the polymeric phases obtained from DITP and DBTP, desorption of DBTP precursors upon annealing, XPS spectra of DITP and DBTP on Au(111) before and after the temperature ramp, XPS spectra of the polymeric phase from DITP after iodine desorption, spectra extracted from the fast-XPS maps showing the different polymerization temperatures for DITP and DBTP, comparison of I 4d core level signal between iodine detached from DITP and iodine deposited from an external source, raw fast-XPS map of DBTP, length histograms for samples obtained from DITP and DBTP with similar growth conditions and similar densities, extraction of kinetic

curves from fast-XPS maps and complementary kinetic curves showing the desorption of the halogens), fit of the kinetic curves and monomer synthesis and characterizations (PDF).

The authors declare no competing financial interest.

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Author Contributions

All authors have given approval to the final version of the manuscript. M.D., P.R. and R.F. conceived the experiments. M.D., O.D., J.U., R.W., T.Di., S.S. and C.S.S. performed the experiments. T.Du. prepared precursor molecules under the supervision by A.N., R.B., X.F. and K.M. The beamline was under the responsibility of M.M. Data analysis was performed by M.D., O.D., T.Di., P.R. and R.F. Manuscript was written by M.D., O.D., P.R. and R.F.

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