On-Surface Radical Oligomerisation: A New Approach to STM Tip-Induced Reactions

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Abstract

Over the past decade, on-surface fabrication of organic nanostructures has been widely investigated for the development of molecular electronic devices, nanomachines, and new materials. Here, we introduce a new strategy to obtain alkyl oligomers in a controlled manner using on-surface radical oligomerisations that are triggered by the electrons/holes between the sample surface and the tip of a scanning tunnelling microscope. The resulting radical-mediated mechanism is substantiated by a detailed theoretical study. This electron transfer event only occurs when $V_s < -3 \text{ V}$ or $V_s > +3 \text{ V}$ and allows access to reactive radical species under exceptionally mild conditions. This transfer can effectively ‘switch on’ a sequence leading to formation of oligomers of defined size distribution due to the on-surface confinement of reactive species. Our approach enables new ways to initiate and control
radical oligomerisations with tunnelling electrons, leading to molecularly precise nanofabrication.

**Introduction**

Free radical polymerisation is the leading industrial method for obtaining polymeric systems and composite materials. The relatively non-specific nature of the free radicals towards monomers makes it one of the most versatile polymerisation methods, but at the same time renders their reactions difficult to control.[1] Indeed, ‘living’ radical polymerisation, where irreversible terminations and transfers are absent while all chains are initiated and grow simultaneously, was considered impossible for many years owing to fast propagation and inevitable radical termination reactions.[2] In the mid-90s, new methodologies that exploit equilibria between growing radicals and dormant species were developed.[3] These approaches differ in the method of radical generation but they all involve the use of a persistent (metallo)radical that reduces the steady-state concentration of propagating radicals and minimizes normal termination of living polymers. The simplicity of adding these reagents to a polymerisation reaction resulted in the ability to synthesize well-defined functionalized (co)polymers.[4,5] However, for a range of applications such as microelectronics, coating technologies and biotechnology, contamination of the final polymer/oligomer by the reagents/additives has become a significant problem and a key limiting factor in their use. Another approach to polymer/oligomer synthesis is tandem reactions, which produce macromolecules with new structures and functions.[6] In particular, since radical reactions are ideal for sequencing, due to the very fundamental reason that the product of every radical reaction is a radical, tandem radical chemistry may serve as a versatile method in radical oligomerisation. These proceed through two or more consecutive steps mediated by the radical’s unpaired electron, and have important advantages over conventional multistep
syntheses such as time- and cost-savings, atom economy, waste reduction and energy consumption.[7] However, they are limited by the reactivity of the active sites which must be well matched so that the product of one chemical transformation does not hamper the overall tandem sequence.

On-surface synthesis under ultrahigh-vacuum (UHV) conditions has attracted considerable attention as a means to generate new and stable molecular structures because it provides an alternative and highly efficient strategy for controlling chemical reactions, and allows for the direct observation or induction of reaction pathways by scanning tunnelling microscopy (STM).[8] However, thus far, the number of C-C bond-forming chemical reactions reported on surfaces remains very limited. In particular, on-surface radical polymerisations have been rarely investigated despite their efficiency in the absence of any catalytic role of the surface while radical species have been observed as intermediates in the case of cross-coupling reactions on surfaces.[9] In the meantime, on-surface oligomerisation represents an attractive method that would benefit from the control provided by the long-range 1D order.[10]

Here, we report the on-surface tandem synthesis of alkyl oligomers on Cu(111), Au(111) and graphite surfaces, mediated by tunnelling electrons/holes from a STM junction. We show, using STM imaging and extensive density functional theory (DFT) calculations, that the on-surface tandem reaction is very likely to be initiated electronically and involves radical intermediates that preferentially form cross-reacted linear oligomer products.

Results

On-surface synthesis

As one-electron reduction of aryl alkyl ethers (e.g., cyanoanisole) has already been shown to produce the corresponding phenoxide anion and the alkyl radical, we chose to use the same type of derivatives in this study.[11] Having previously obtained bilayered networks of the
aryl alkyl ether CDB-OC10 (Figs 1a, S1 and S2) on silicon [12] or ionic alkali halide surfaces [13] we modified the procedures for the adsorption of the same aromatic molecule on Cu(111), Au(111) and highly oriented pyrolytic graphite (HOPG) surfaces under UHV. In order to examine the influence of side chains, we also synthesized shorter aryl ether as well as aryl alkyl building blocks (CDB-OC3 and CDB-C12, respectively, Figs 1a, S3 and S4). These compounds are based on a triphenyl core terminating with two cyano moieties and further core-substituted by two lateral ether or alkyl chains (Fig. 1a). The distance between the two cyano groups was calculated to be 1.65 nm and the side chain lengths in CDB-OC3, CDB-OC10 and CDB-C12 were 1.43, 3.18, and 3.40 nm, respectively.

Figure 1b shows a high resolution STM image, recorded at 110 K, after the deposition of CDB-OC10 by thermal sublimation under ultra-high vacuum conditions on a Cu(111) substrate held at room temperature. A 2D periodic network constituted of bright-aligned protrusions (length: 1.6 ± 0.1 nm) surrounded by slightly darker rods (length: 3.2 ± 0.2 nm) was observed. The different periodicities between bright lines or between darker features are described in Fig. S5. In accordance with the features of CDB-OC10, the bright protrusions can be attributed to the triphenyl cores of CDB-OC10 and the darker paired rods correspond to the interdigitated C10 alkyl chains of two CDB-OC10 molecules involved in two adjacent lines (Fig. 1b) [12,14]. This result is representative of those obtained by repeated experiments for the bias voltage between -3 V to +3 V. Notably, at the bias voltage of -3 V we observed a remarkable modification of the CDB-OC10 molecules in STM images.
Figure 1 | Structure and supramolecular organization on a Cu(111) surface. a) Chemical structures and calculated lengths of 1,4-di(4’,4”-cyanophenyl)-2,5-bis(decyloxy)benzene (CDB-OC10), 1,4-di(4’,4”-cyanophenyl)-2,5-bis(propyloxy)benzene (CDB-OC3) and 1,4-di(4’,4”-cyanophenyl)-2,5-bis(dodecyl)benzene (CDB-C12). b) STM image of the supramolecular network obtained after the deposition of CDB-OC10 on a Cu(111) surface. ($V_s$= -1.5 V, $I_s$= 1.01 nA, 110 K, 15×15 nm$^2$). Inset: the superimposed model of a CDB-OC10 molecule.

The STM image of a step edge island of the CDB-OC10/Cu(111) network acquired at 110 K and at the sample bias of -2.6 V (Fig. 2a) indicated that all aromatic molecules are intact as
they exhibit their typical cross-shape. However, when a bias voltage of -3 V (detailed procedure in Fig. S6) was applied for 1 second over the connection of triphenyl cores and alkoxy chains of the CDB-OC10 molecules of the step edge island (Fig. 2a and Fig. S7), the resulting STM image of the same region showed that the alkoxy chains of CDB-OC10 molecules were missing (Fig. 2b). By scanning the region of interest, we observed two additional rod-like features with a length of 1.4 ± 0.1 nm confined between four intact CDB-OC10 molecules (white arrows Fig. 2c), corresponding to two C_{10}H_{22} chains adsorbed in pores of the supramolecular CDB-OC10/Cu(111) network (enlarged view in Fig. S7c). These experiments clearly indicate that the CDB-OC10 derivatives can be cut with atomic precision by applying a pulse voltage of -3 V at 110 K on a Cu(111) surface and that the produced alkanes are still adsorbed on the surface.
Figure 2 | Results of application of variable voltage to CDB-OC10 on Cu(111). a) STM image ($V_s$ = -2.6 V, $I$ = 1.00 nA, 110 K, 30×30 nm$^2$) of the obtained supramolecular network after the deposition of CDB-OC10 on a Cu(111) surface. The STM tip was then moved step by step, along the dash white arrow, at $V_s$ = -3 V. b) STM image ($V_s$ = -2.6 V, $I$ = 1.00 nA, 110 K, 30×30 nm$^2$) of the same area. All bright rods extending out of the supramolecular network have been broken. c) STM image ($V_s$ = -2.6 V, $I$ = 1.00 nA, 110 K, 30×30 nm$^2$) of the same area showing two C10 alkane chains (white arrows) confined between intact CDB-OC10 molecules. d) STM image ($V_s$ = 0.8 V, $I$ = 1.01 nA, 110 K, 16×14 nm$^2$) showing a supramolecular network constituted of parallel bright rods with different lengths. e) Adsorption model showing the coexistence of intact CDB-OC10 molecules and self-assembled alkanes.

With these results in hand, we were then interested in obtaining further insight into the reaction behaviour by scanning the CDB-OC10/Cu(111) network at 110 K at $V_s$ = -3 V. Thereafter, the STM-tip was moved on an uncovered zone of the Cu(111) surface, which was scanned at $V_s$ = 1.5 V and 110 K. We found that the complete area was covered by strips consisting of parallel and continuous rods (Fig. 2d). Although short rods (1.2 ± 0.1 nm) were rarely observed, the length of most of these rods varied from 2.5 to 3.6 nm. Based on the systematic analysis of over 20 STM images, the following size distribution was obtained: 82% of rods measured 3.6 ± 0.2 nm, 9% 2.5 ± 0.2 nm, 8% 4.9 ± 0.2 nm, and 1% 1.2 ± 0.1 nm. These rods can be ascribed to the alkane oligomers adsorbed on the Cu(111) surface (Fig. 2e).[15] The number of carbon atoms in adsorbed alkanes was 10, 20, 30 and 40 for stick lengths of 1.2 ± 0.1, 2.5 ± 0.2, 3.6 ± 0.2 and 4.9 ± 0.2 nm, respectively. The most frequent alkane contained 30 carbon atoms while the least commonly observed fragment contained only 10 carbon atoms. When the same set of experiments is carried out with a positive sample bias voltage, $V_s$, the formation of alkanes is only observed if $V_s$ is > +3 V (Fig. S8). Therefore, these experiments revealed that the cleavage of C-O bonds of CDB-OC10 molecules adsorbed on a Cu(111) surface only occurs if $V_s < -3$ V or $V_s > +3$ V.

To gain further insight into the reaction mechanism, three other experiments were conducted: i) Au(111) and HOPG were used as less reactive surfaces than Cu(111) to rule out
any catalytic role of the surface; ii) the length of the alkyl chain of the starting aryl alkyl ether derivative was shortened in order to favour the formation of more reactive radical alkyl groups; iii) the ether function was replaced by a much less reactive alkyl group in order to investigate the reaction behaviour of these aryl compounds in greater detail.

Firstly, we investigated the role of the surface by depositing CDB-OC10 molecules on Au(111), a more benign noble metal surface, and on HOPG, a completely inert surface, both at 110 K. In all cases, we observed the formation of supramolecular networks constituted of intact CDB-OC10 molecules. The dealkylation process of these molecules on Au(111) or HOPG only occurs if $V_s < -3$ V or $V_s > +3$ V. On both surfaces, the subsequent formation of supramolecular networks of alkanes is observed unambiguously (Figs. S9 and S10). As C-O bond activation occurred even on HOPG at low temperature, these results clearly demonstrate the absence of any catalytic role of the surface. In addition, it also proves that the molecule-surface interaction is one of the key parameters, which determines the value of the threshold of bias voltage for each molecule-surface combination.[16]

We then investigated the deposition on a Cu(111) surface of the 1,4-di(4',4''-cyanophenyl)-2,5-bis(propyloxy)benzene (CDB-OC3, Fig. 1a) derivative which contains short propyl side chains. As the side chains in CDB-OC3 are shorter (and also more mobile and more reactive)[17] than in CDB-OC10, molecule-molecule interactions are much weaker. Therefore, the formation of supramolecular networks is mainly governed by molecule-surface interactions, due to the presence of the cyano groups, enabling the formation of four different networks (Fig. S11). As previously described for other molecule/surface combinations (vide supra), the dealkylation process of CDB-OC3 molecules on Cu(111) surface only occurs if $V_s < -3$ V or $V_s > +3$ V. After the cleavage of the corresponding C-O bonds, a continuous scan with a bias voltage of -0.8 V at 110 K of these networks led to the observation of a small metal surface covered by parallel rods, whose length varied from 1.0 ± 0.1 to 4.8 ± 0.4 nm
The clear observation of rod presence can also be attributed to alkane formation. A close examination of the statistical distribution of length showed that alkanes containing 18 and 21 carbon atoms (i.e., hexamers and heptamers, respectively) were mainly obtained (Fig. S12d). By contrast, among the products of the CDB-OC10 reaction, the longest alkane corresponded to a tetramer containing 40 carbon atoms. This is in accordance with previous observations that the reaction pathway is initiated by a radical process and that short radical chains are more mobile and reactive than long radical chains.[17]

We then sought to test the applicability of the presented procedure by depositing the 1,4-di(4’,4’’-cyanophenyl)-2,5-bis(dodecyl)benzene derivative (CDB-C12) on Cu(111). While dealkylation of aryl alkyl ethers was previously reported in the literature,[18] aryl alkanes are known to be inert compounds. For instance, the C(aryl)-C(alkyl) bond was determined to be highly robust, even upon thermal annealing on a reactive surface.[15a] Once again, the dealkylation process of CDB-C12 only occurs if $V_s < -3.1 \text{ V}$ or $V_s > +3.1 \text{ V}$. In the resulting STM images acquired at 110 K (Fig. S13), we observed two types of supramolecular networks such as in the case of CDB-OC10 on Cu(111). The first one was constituted of intact CDB-C12 moieties, which are easily recognizable thanks to their characteristic cross-shape (lower part of Fig. S13b). The second one was composed of multiple parallel rods, with a length varying from $1.0 \pm 0.1$ to $3.3 \pm 0.3 \text{ nm}$ (upper part of Fig. S13b). These features are attributed to alkane molecules containing from 12 to 36 carbon atoms, which are self-assembled on the Cu(111) surface. This experiment demonstrates that the C(aryl)-C(alkyl) bond in CDB-C12 molecules is only activated if $V_s < -3.1 \text{ V}$ or $V_s > +3.1 \text{ V}$ on the Cu(111) surface at 110 K. Also, the production of alkyl derivatives occurs on this surface, with the formation of the corresponding C36 alkane.
DFT investigations

To gain further insight into the bond activation process experimentally observed, the density of states of the initial state CDB-OC3 / Cu(111) interface is analysed using the DFT-based orbitals-projected Density of States (pDOS) (Fig. S14) and the thermodynamics of C-O dissociation process is evaluated using DFT framework in vacuum and under electric field (See Fig. S15 and Method).

**Figure 3** | DFT simulations of the C-O bond dissociation process. a) DFT-based chemical pathway of the first dissociation of one CDB-OC3 molecule adsorbed on the Cu(111) producing the intermediate [RAD_CDB] resulting from the removal of one C3 radical chain which then binds onto the substrate [RAD_C3]. The snapshots are the results of DFT geometry optimizations. b) Dissociation enthalpy in eV under no constraint (value as X =0) and as a function of two independent external stimuli: the electric field (black curve) and the charging procedure (red curve).
The LUMO resonance of **CDB-OC3** molecule is peaked at +1 eV on Cu(111) and mainly localized on the triphenyl core of the molecule. The HOMO resonance is peaked at -1 eV on Cu(111) (Fig. S14). The first C-O dissociation process of adsorbed **CDB-OC3** on Cu surface was modelled using different supercell systems (Fig. 3a): the reactant **CDB-OC3**, the two products (*i.e.* RAD_CDB and RAD_C3) and the bare Cu surface. The dissociation enthalpy in vacuum equals differences between total energies E of all systems (*i.e.* $E(\text{CDB-OC3}) - E(\text{RAD}_{\text{CDB}}) - E(\text{RAD}_{\text{C3}}) - E(\text{Cu})$) and its value of +1.20 eV is displayed at zero X axis in the energy plot of Fig. 3b. Next the distinct influence of two stimuli accounting for electric-field and electron inductions is rationalized: one mimicking the presence of the electric field equivalent to the voltage pulse (*via* the procedure described in Fig. S15) and the second modelling the charging (*i.e.* adding and subtracting one electron on the **CDB-OC3** molecule and its offsprings RAD_CDB). The dissociation enthalpy under electric field corresponds to the total energy E of all systems including an electric field, while the dissociation enthalpy of charged **CDB-OC3** results from charged **CDB-OC3** and RAD_CDB systems but neutral RAD_C3 and Cu systems. As a result, Fig. 3b shows that the first dissociation enthalpy of 1.20 eV in vacuum is lowered by 10% similarly in the case of the anionic species (1.10 eV, red curve) and of a positive applied electric field corresponding to a positive bias (1.08 eV, black curve). By contrast a negative electric field (corresponding to a negative bias) is increasing by 5% the endothermicity to +1.27 eV (minor effect). The most detrimental effect comes from the cationic species with the highest enthalpy difference of +1.35 eV. Based on these model calculations we can evaluate separately the effects of the two stimuli: they remain modest but the electron stimulus has a more important role.

**Discussion**

The formation of oligomeric alkanes from aromatic species containing only ether or alkyl side chains as precursors is previously unreported in the literature. The resulting mechanism
should imply at least two steps: (i) the activation of the C-O/C-C bonds of the aromatic precursors at a fixed bias voltage and then (ii) the on-surface oligomerisation of the generated species. For instance, the activation mechanism of C-O bonds in alkyl aryl ether derivatives has been deeply investigated in solution [11] and very recently described by Yang et al. on noble metal surfaces. [18] These authors suggested that the dealkylation process is based on a thermally-induced intramolecular prototropy of a hydrogen atom from the alkyl chain to the oxygen atom of the ether function. In solution, the dealkylation of aryl alkyl ethers can originate from a reduction (through an electron transfer [11]), or can be catalysed by a Lewis or Brønsted acid [19] or by organometallic complexes (oxidative addition [20]). In our experiments, it is reasonable to rule out that the mechanism is based on a catalyst because no external catalytic species were introduced on the surface. As the dealkylation reaction takes place even at low temperature, a thermally-assisted mechanism is also unsuitable. By contrast, controlled excitations of molecules can be performed by using inelastic-electron-tunnelling (IET) [21] or electric-field [22] induced manipulation processes. In an IET manipulation, low energy tunnelling electrons are injected to the molecule located on a surface by positioning the tip above the target. The tunnelling electron energy is transferred to a molecule through an adsorbate-induced resonance state. The dissociation of the molecule occurs if the transfer-energy is higher than the dissociation barrier. In our work, excitation of the adsorbate results in excitation of specific chemical bonds and therefore in selective C-O or C-C bond cleavage. In addition, the resulting dealkylation process only occurs if \( V_s < -3 \) V or \( V_s > +3 \) V, without any role of the polarity (Fig. S8). All these features are typical of an IET process. [21] When chemical reactions are stimulated by the tunnelling current in a STM junction, different mechanisms are proposed to support such bond activation. [23, 24] On the basis of experimental results and simulations (i.e. C-O/C-C bond dissociation occurring at negative and positive bias voltage), we can state that these C-O/C-C bond cleavages are governed by
tip-induced processes, such as electron- (at positive bias voltage) or hole- (at negative bias voltage) attachment in unoccupied and occupied molecular orbitals of adsorbates, respectively.[24]

It is worth noting that after C-O bond activation, the resulting phenoxide moieties were rarely observed on the STM images (Fig. S16). This can be explained by their low adsorption energies on the Cu(111), leading to their desorption. Concerning the alkyl chains, if the yield of cleavage is 100%, only 17% of C10 chains are found on the surface near the cleaved molecules (Fig. 2). However, the alkane derivatives appear again by scanning zones of uncovered Cu(111) surface (Fig. S17) or covered by supramolecular network of intact CDB-OC10 molecules at V_s = -1.4V (Fig. S18a-b). This feature indicates that the STM tip can act as a reservoir of C10 alkyl radicals, which can be released on the surface. If the radicals are delivered on the Cu(111) surface covered by the supramolecular network of CDB-OC10 molecules, only C10 alkanes are observed, proving that polymerization occurs on the surface. When the radicals are released on the uncovered Cu(111) surface, they are free to diffuse on the surface (Fig. S18c-h). Also, as an alkyl radical is generated by the bond activation process, this first step can be considered as the initiation of a radical oligomerisation (Fig. 4a-b). The chain growth stage is regulated by radical formation rate such as the propagation step of a radical oligomerisation (Fig. 4c). In contrast to oligomerisations in solution, the alkyl radicals have to diffuse in order to react, limiting the possibilities of the substrates to react and explaining why only linear alkanes are observed. When the alkanes are long, the chain growth can be halted by three possible termination processes (Fig. 4d). As residual hydrogen gas is present in the UHV chamber, the termination step can occur by the reaction of radicals with H_2. The occurrence of such types of side reactions might explain the fairly modest lengths observed for the final alkanes. However, in agreement with previous observations, we considered that the 2D confined geometry could also favour some reactions that are not
usually observed. Due to the unique space confinement, the formation of linear oligomers of similar molecular weights can be controlled. This finding is consistent with the statistical analysis of the size distribution of alkanes adsorbed on Cu(111) surface.

**Figure 4** | C-O bond activation and cleavage followed by oligomerisation of the ensuing alkyl radicals on a Cu(111) surface. a) IET process by electron attachment leading to the formation of a radical-anion at $V_s > +3$ V. b) C-O bond cleavage leading to the formation of a phenoxide anion and an alkyl radical. This step is the initiation step of the radical oligomerisation of alkyl chains. c) propagation of the radical oligomerisation. A chain-transfer reaction of radical leads to the growth of the length of produced alkanes. d) Termination of the radical oligomerisation by various mechanisms: by combination with hydrogen present in the UHV-chamber (residual pressure of $10^{-11}$ mbar), by combination between two radicals or by disproportionation.

In summary, we have used STM under UHV conditions and certain voltage application to initiate the synthesis of alkyl oligomers. All these experiments clearly demonstrate that the observed transformations are triggered by inelastic electron tunnelling and do not require any
catalytic role of surfaces. This allows the formation of tip-induced radicals that are able to cross-react in a controlled manner without adding any additives to produce alkyl oligomers. We used DFT calculations to support the proposed electronically-triggered radical anion formation as the mechanism for the initiation of the process. We found that the surfaces have no catalytic role in the scission process, and that both site-specific C-O and C-C bonds can be cleaved to produce the radical intermediates. The origin of the experimentally-observed selectivity towards oligomer products has been attributed to the 1D restriction of the reactive species along the surface. This tip-induced radical oligomerisation is a major step towards the fabrication of molecular electronic devices and novel nanomaterials.

**Methods**

**Materials.** All reagents were purchased (Sigma Aldrich) and used as received. Detailed methods are described in supplementary information.

**STM experiments.** STM experiments were performed in an ultrahigh vacuum chamber with a base pressure lower than 2·10^{-10} mbar equipped with a variable temperature Omicron Scanning Tunnelling Microscope. STM images were acquired in a constant current mode at 110 K or at room temperature. All the molecules were deposited from a quartz crucible at 443 K. The Cu(111), Au(111) or HOPG substrate was kept at room temperature during the sublimation. Each image process was carried out using WSXM software.[25]

**DFT calculations.** *Ab-initio* calculations have been performed in the framework of density functional theory as implemented in the VASP code.[26] To model the CDB-OC3/Cu(111) interface, a 4-layer slab in a 7x7 periodic supercell embedded in about 18 Å of vacuum space was employed. Ion-electron interaction was described with PAW method and exchange and correlation energy was modeled with GGA-PBE.[27] The atomic positions of the two topmost
metallic layers, and the molecule were relaxed until forces were smaller than 0.05 eV/Å. We considered the standard value of 400 eV energy cut-off in the plane-wave expansion restricted to the Gamma point for the BZ sampling of the supercell for structures and energies. An important tool is the projected density of states (PDOS) of the chemisorbed system onto a molecular orbital, MO, with MO is the free-molecule state onto which the density of states is projected. The MO is calculated for the free molecule distorted to its chemisorption geometry. The PDOS is informative of the molecular character of the chemisorbed system and has been successfully used a previous study of surface reactivity.[28]

To model the voltage induction, an external uniform electric field is introduced perpendicular to the slab using the method proposed by Neugebauer and Scheffler [29] and implemented in VASP (Fig. 3). Finally, the adsorbed CDB-OC3 and the first dissociation product been both charged to mimic the reduction (or oxidation) by one electron.

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Author contributions
G.Z., Y.M., J.J., S.L., M.F., and F.P. performed the experiments and M.-L.B simulated the systems. C.M.T. and F.C. wrote the manuscript with support from the co-authors. All authors analysed the data, discussed the results and commented on the manuscript.

**Additional information**

The authors declare no competing financial interests. Supplementary information is available for this paper at. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to F.C. and C.M.T.

**References**

[1] For instance, almost 40% of all polymers produced in the United States are produced by this mechanism.


[9]  


