Carbon dioxide as a solvent for synthesis and processing

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Abstract

Supercritical carbon dioxide is emerging as a potentially interesting solvent for synthesis and processing under environmentally benign conditions. In this paper we address three features of the use of carbon dioxide where the particular benefits of the solvent realise different consequences from those observed in conventional organic solvents.
We first examined the dipolar cycloaddition of nitrile oxides to alkenes and alkynes and show that the regiocontrol obtained can be tuned according to the solvent density. We then address the applications of the Suzuki cross-coupling reaction using a solid phase supported palladium catalyst to make conjugated aromatic materials. Extension to the use of conventional solvents allows the synthesis of CO_2-philic oligomeric fluorene derivatives. Finally, we demonstrate the patterned deposition of a fluorinated polymer onto a patterned silicon wafer substrate.

Nitrile Oxide Cycloadditions in Supercritical Carbon Dioxide

Apart from the Diels-Alder reaction,[1, 2] there has been little reported on cycloaddition chemistry in $scCO_2$. 1,3-Dipolar cycloadditions are an important class of cycloadditions, typically giving rise to 5-membered heterocycles, many of which are of pharmaceutical interest. In the present study, eactions of nitrile oxides and olefins were examined in $scCO_2$. The scope of nitrile oxide cycloadditions in $scCO_2$ was exemplified in high yielding reactions of mesitonitrile oxide with numerous alkenes and alkynes bearing various functional groups.

Synthesis of fluorine-containing polyfluorenes

Many factors determine whether or not a polymer shows solubility in liquid or supercritical CO_2. Amongst them are the polymer backbone architecture, the amount and the nature of CO_2-philic groups and the distribution of such groups within the polymer. In order to find the optimal structure of a CO_2 soluble polyfluorene and its content of CO_2-philic fluorine, the first aim was to synthesise a range of homo- and copolymers with various degrees of fluorination and then carry out solubility tests in supercritical carbon dioxide. While one possibility of varying the fluorine content is altering the length of the fluorinated side chain, another approach is the synthesis of copolymers containing fluorinated as well as non-fluorinated units (Fig. 2).

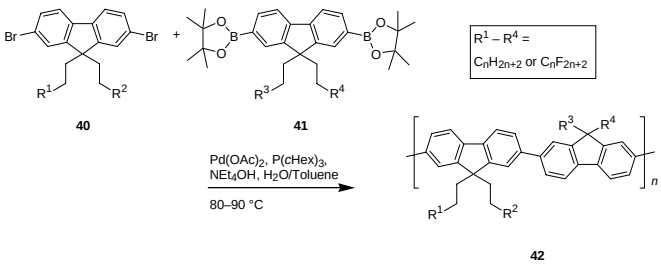

Fig. 1: Synthesis of partially fluorinated polyfluorenes **42** by Suzuki polymerization.

The polymerization reactions were carried out under the conditions optimized for the synthesis of alkyl substituted polyfluorenes. The polymers produced in this way were quite soluble under the reaction conditions if they contained at least 25% of non-fluorinated alkyl substituents. Any higher degree of fluorination led to the precipitation of polymer that then proved insoluble in all common solvent. A possible reason for the lack of solubility of the polymers is a high degree of crystallinity caused by interactions of the fluorinated side chains as well as the stiffness of the polymer. In order to make the polymers more flexible, a series of linkers was introduced into the backbone. Since these linkers break down the conjugation of the resulting polymers, it is important that a minimum conjugation length is maintained to allow efficient electroluminescence. This work shows sufficient promies to justify further research.

Patterned Deposition in sc Carbon Dioxide

Considerable progress has been made in recent years in using compressed CO_2 for deposition of fluorinated coatings on surfaces . One particularly attractive application is in advanced photolithography where there has been much interest in submicron feature sizes using fluoropolymers which are transparent at 157 nm. A preliminary study into the potential use of compressed CO_2 as an alternative solvent for inkjet printing is presented. This technique should have many applications in the deposition of organic and polymeric materials for optoelectronic devices. Preliminary results were carried out using a 10 cm^3 stainless steel high pressure reaction vessel equipped with a sapphire window.

Typical procedure for deposition of a polymer in CO_2 onto a patterned Si wafer

A solution of fluorolink® in compressed CO_2 was prepared in a 500 cm^3 reaction vessel as follows. Fluorolink® (0.5 g) was charged into the vessel and then sealed. Liquid carbon dioxide was withdrawn from a supply cylinder (BOC, CP grade; 99.995%), passed through the chiller (2) and compressed by the air driven liquid piston pump (Haskell MCPV-71). The chiller was required to avoid cavitation of the pump. The CO_2 stream was then heated to the desired conditions by the use of heat exchanger and directed to the reaction vessel.

The pressure was raised by the pump to 100 bar and maintained at this condition by the back pressure regulator (Go Products, Model PR-57). The vessel was located within an insulated air bath, which was maintained at a constant temperature of 35°C (±0.1 ºC) during the process. The temperature was recorded using type K thermocouples (RS Electronics) encased in 316 stainless steel and displayed on a temperature indicator (T200, RS Electronics). The pressure was measured by a pre-calibrated pressure transducer and a dedicated indicator (Druck PTX 52100 and DPI 262, respectively), which had an accuracy of ±0.3 %. After a short equilibration time (10 mins) in which the polymer became solubilized in the CO_2, the cell was vented via a heated nozzle (length 10 cm; diameter 127 m) and the contents were delivered onto a patterned Si wafer which was held at a distance (*d*) 3 cm away from the nozzle outlet for a period of 30 s. Pressure drop within the vessel during spraying was minimized by increasing the stroke rate of the piston pump to maintain the pressure within the system. The patterned Si wafer was prepared using UV mask lithography on alkyltrichlorosilane self-assembled monolayers (SAMs) at the Base Technology Centre, Seiko-Epson, Suwa, Japan.

The following parameters were altered in order to obtain the best results for deposition: the polymer {poly(1*H*,1*H*,2*H*,2*H*-perfluorooctyl acrylate), poly(1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate) and Fluorolink®}, the solution concentration (0.02 - 0.1 wt%), temperature within the reaction vessel (25 – 35 °C), time for deposition (5 – 30 s), the nozzle temperature during deposition (25 – 35 °C), nozzle dimensions (length 5 – 10 cm; diameter 127 m) and finally the distance (*d*) from nozzle outlet to wafer (3 – 10 cm).

Our results suggest that better patterns are observed after deposition by using more concentrated solutions at 35 °C, lowest possible nozzle diameter and nozzle lengths of 10 cm. Under these conditions we were able to obtain good resolution with 5 m dot sizes. Improved deposition also occurred when the distance between the Si wafer and the nozzle was reduced. At lower temperatures precipitation of the polymer occurred at the tip of the nozzle. Increasing the nozzle temperature reduced the amount of precipitation. When nozzles with a larger capillary diameter were used, the polymer was deposited unevenly leading to poor pattern replication. Similarly when the distance between the wafer and nozzle was increased, poor pattern replication was observed. Improved deposition was achieved when the duration of the experiment was extended to 30 s. This is presumably due to the improved mass transfer from the solution onto the wafer allowing a more even distribution of the polymer solution.

References

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