



EXPEDIENTE	IMAMCK/2016/1
ACRÓNIMO	CO2PUSHOE
PROGRAMA	PROYECTOS DE I + D PROPIA
TÍTULO DEL PROYECTO	POLIURETANOS SOSTENIBLES OBTENIDOS A PARTIR DE DIÓXIDO DE CARBONO PARA LA INDUSTRIA DEL CALZADO

Entregable E1.1. RECAPITULACIÓN BIBLIOGRÁFICA

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1. Descripción del entregable

En este paquete de trabajo se ha realizado una búsqueda bibliográfica actualizada al momento de inicio del proyecto (revistas científicas y técnicas, patentes, etc.) con objeto de mejorar la base científica sobre la que se sostiene la investigación.

2. Trabajo realizado

Concretamente, se ha realizado una recapitulación bibliográfica actualizada y relativa a poliuretanos sostenibles basados en CO₂, sus rutas de polimerización, reactivos procedentes de fuentes renovables y empresas proveedoras, consultando las siguientes fuentes de información, disponibles en el Dpto. de biblioteconomía y documentación de INESCOP:

- Bases de Datos Electrónicas.
- Revistas especializadas, técnicas o científicas, que publican tendencias, novedades, desarrollos, resultados de investigaciones destacadas, etc.
- Memorias de congresos, ponencias, etc.

A continuación se muestra un resumen de la recapitulación bibliográfica efecuada:

LIBROS:

- M. Aresta. "Carbon Dioxide as Chemical Feedstock". Chapter 8: "Polymers from carbon dioxide: polycarbonates, polythiocarbonates and polyurethanes". D.J. Darensburg., J.R. Andreatta, A.I. Moncada (2010). 213-244.
- L. F. Vega y col. "Usos del CO₂: un camino hacia la sostenibilidad". Plataforma Tecnológica Española del CO₂ (PTECO₂). 2013.
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- "Szycher's Handbook of Polyurethanes". Szycher, M. Boca Raton, FL. CRC Press (1999).
- J.M. Martín, A.C. Orgilés. "Curso sobre Poliuretanos" Ed. INESCOP, Alicante, España, (1994).

ARTICULOS CIENTIFICOS:

- "The global PU industry 2013/2014 review and forecast". *PU Magazine* 11, 1, 25-31. 2014.
- M.A. Corcuera, L. Rueda, A. Saralegui, M.D. Martín, B. Fernández-D'Arilas, I. Mondragon, A. Eceiza. "Effect of diisocyanate structure on the properties and microstructure of polyurethanes based on polyols derived from renewable sources". *J. Appl. Polym. Sci.*, **122**(6) (2011) 3677-3685.
- C. Bueno Ferrer, E. Hablot, F. Perrin Sarazin, M. C. Garrigós, A. Jiménez, L. Averous. "Structure and Morphology of New Bio-Based Thermoplastic Polyurethanes Obtained From Dimeric Fatty Acids". *Macromol. Mat. & Eng.*, **297**(8) (2012) 777-784.
- Z.S. Petrović, "Polyurethanes from Vegetable Oils". *Polym. Rev.*, **48**(1) (2008) 109-155.
- "CO₂ as a polyol intermediate –the dream becomes a reality". *PU Mag*, 10, 4. Aug-Sep (2013) 236-239.
- "Manufacturing innovative materials for CO₂ capture and reuse". *Carbon Capture Journal*, 36, 11-12. nov/dec 2013.
- "More than hot air". *C&EN Chemical & Engineering News*. Nov nº 4, 20-22. 2013.

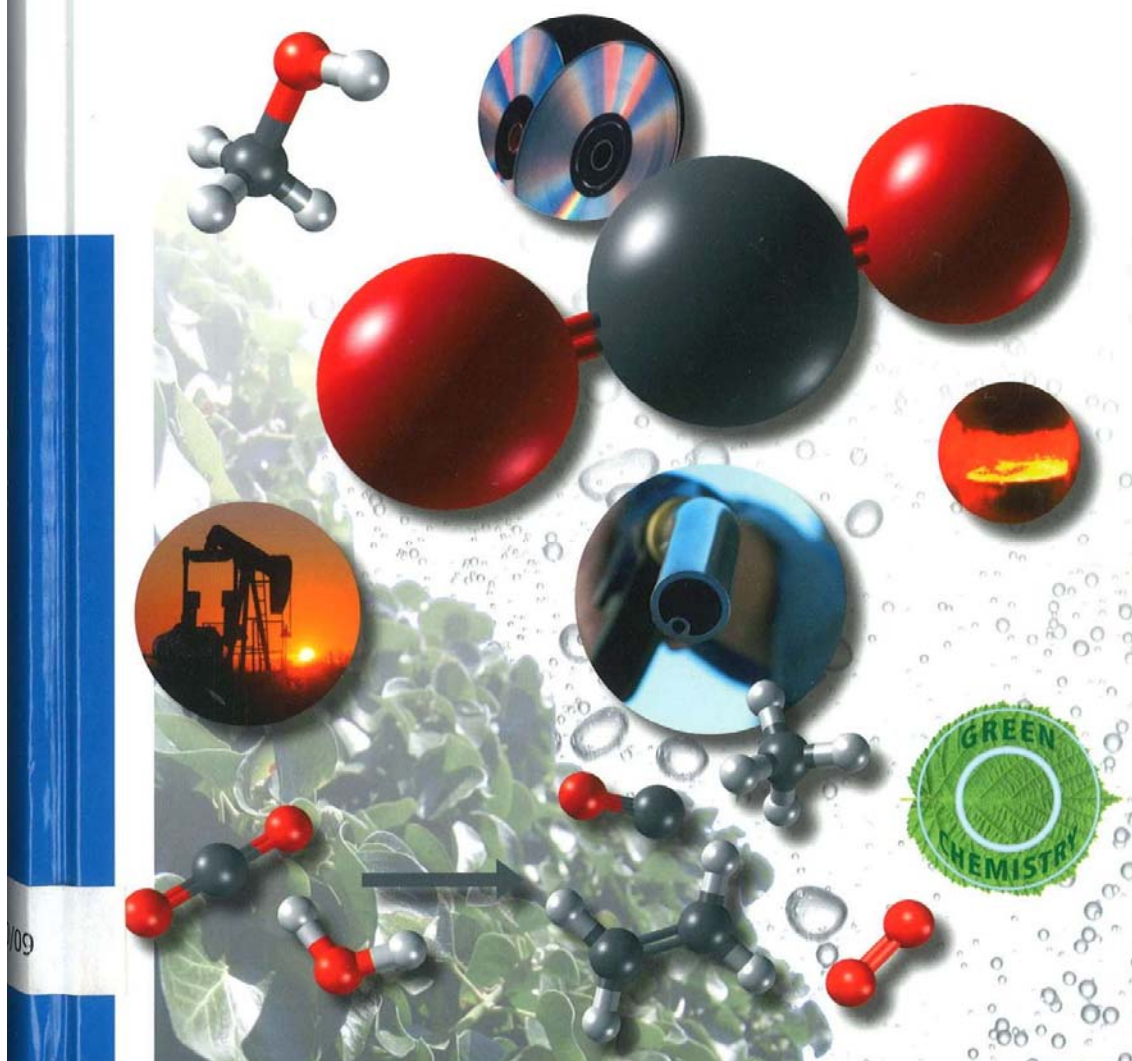
PROCEEDINGS DE CONGRESOS:

- P. Shepard. "Overview of Novomer's CO₂-based Polyol Technology Platform" Sustainable Polyurethanes Conference. Amsterdam, 7-8 may (2013).
- C. Gürtler. "Dream Production - CO₂-based polyols (polyetherpolycarbonatepolyols) with improved sustainability". Sustainable Polyurethanes Conference. Amsterdam, 7-8 may (2013).
- S. Waddington. "Carbon Dioxide-Based Polycarbonate Polyols for Polyurethane Systems; Commercial Applications of CO₂-based Polyols" 3rd Conference on Carbon Dioxide as Feedstock for Chemistry and Polymers. Haus der Technik, Essen, Germany. 2-3 December. 2014.
- S. Waddington. "CO₂ based Polyols give enhanced properties in Reactive Hot melts". Proceedings of FEICA European Adhesive & Sealant Conference and EXPO 2014. Berlín.

Edited by Michele Aresta

WILEY-VCH

Carbon Dioxide as Chemical Feedstock

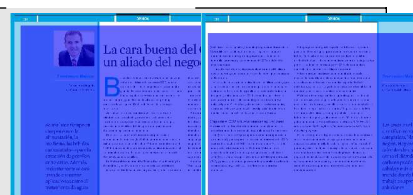


Usos del CO₂: un camino hacia la sostenibilidad



2013

pteco₂
Plataforma Tecnológica Española del CO₂



Francesco Maione

Consejero delegado
de Carburos Metálicos

Se usa hace tiempo en campos como la alimentación, la medicina, las bebidas carbonatadas o para la extracción de petróleo, entre otros. Además, recientemente se está usando en nuevas aplicaciones como el tratamiento de aguas

La cara buena del CO2: un aliado del negocio

Bastante a menudo leemos o vemos noticias que señalan al dióxido de carbono (CO2) como el causante de efectos perjudiciales para nuestro planeta. En consecuencia, este gas no tiene una buena reputación. Pero no todo en la ciencia es blanco o negro, y por ello en estas líneas me propongo convencerles de que el CO2 también puede ser un gas beneficioso.

Además de ser un elemento clave en el proceso de fotosíntesis de las plantas, cosa que a todos nos viene rápidamente a la cabeza, está demostrado que este gas también es muy útil en distintos procesos químicos con destacadas aplicaciones industriales.

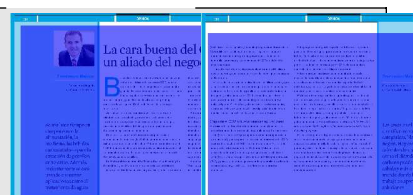
En efecto, se usa hace tiempo en campos como la alimentación, la medicina, las bebidas carbonatadas o para la extracción de petróleo, entre otros. Además, recientemente el CO2 también se está usando en nuevas aplicaciones como el tratamiento de aguas, la energía, los nuevos materiales o la desinsectación de semillas.

En todos estos sectores el CO2 se aplica actualmente y ha demostrado ya sobradamente sus cuantiosos beneficios. Hay sectores donde su uso es muy evidente, mientras que en

otros, como el de la alimentación, su aplicación puede sorprender. No obstante, numerosos proyectos llevados a cabo por centros de investigación de referencia han demostrado la gran utilidad del CO2 en el campo de la alimentación. Si nos fijamos en los hábitos actuales de nuestra sociedad, cada vez es mayor el interés por los productos frescos y naturales, aunque el ajetreado ritmo de vida que llevamos nos hace recurrir muchas veces a productos envasados o precocinados.

Buscamos alimentos con pocos aditivos o ninguno, si es posible, y que conserven todas sus propiedades nutritivas durante el máximo tiempo posible. Para lograrlo, se requiere un envasado adecuado y especial que se denomina envasado en atmósfera modificada, también conocida como envasado en atmósfera protectora (EAP). Es en este proceso donde el CO2 juega su papel, junto a otros dos gases, el nitrógeno y el oxígeno, que se combinan en distintas proporciones en función del alimento. El resultado son, por ejemplo, las ensaladas listas para comer o la carne que encontramos envasada en el supermercado.

Procesos como éste son llevados a cabo por Carburos Metálicos junto con instituciones de prestigio y de renombre en nuestro país, como por ejemplo la que tenemos con el Irta



(Instituto de Investigación y Tecnología Agroalimentarias de la Generalitat de Catalunya), gracias a un pionero acuerdo marco de colaboración público-privado para impulsar y desarrollar procesos y aplicaciones del CO2 en el ámbito agroalimentario.

Para el desarrollo de estos proyectos Carburos Metálicos cuenta, además, con un centro propio de investigación ubicado en Barcelona.

El éxito de los proyectos realizados en los últimos años, que se han materializado en innovadoras aplicaciones industriales centradas en las áreas de agricultura, alimentación, tratamiento de aguas y aplicaciones de CO2, ha llevado a que el centro haya sido reconocido internamente por nuestra empresa matriz, el grupo Air Products, al que pertenece la compañía, como uno de los seis centros de investigación de referencia mundial, siendo uno de los dos que están en Europa.

Capturar el CO2 y buscar nuevas aplicaciones

El dióxido de carbono tiene también un papel clave en otro proyecto innovador que se está desarrollando actualmente en Telde (Gran Canaria) y que supone una mejora importante en sostenibilidad, ya que permitirá reducir las emisiones de CO2 a la atmósfera hasta en 8.500 toneladas cada año. Se trata del acuerdo de colaboración entre Carburos Metálicos y la compañía Vidrieras Canarias, por el que nuestra planta en Telde (Gran Canaria) dejará de quemar petróleo para producir CO2, y pasará a utilizar el gas sobrante que emite actualmente la chimenea anexa de la planta vidriera en su proceso productivo.

Este proyecto hará posible que la de Telde sea la primera planta en el mundo que, gracias a una innovadora tecnología, trate el CO2 sobrante de una empresa vidriera y lo utilice a nivel industrial para el sector alimentario. Además, este proceso permitirá reducir las emisiones de CO2 de la compañía y aumentar la eficiencia energética de la misma.

Esta ambiciosa iniciativa es una muestra de cómo la innovación ha ido ligada a la capacidad de ofrecer soluciones eficientes que contribuyan a aumentar la productividad industrial y, que a la vez, ayuden a mejorar la sostenibilidad de nuestros clientes con respecto al medio ambiente.

Podría continuar explicándoles ejemplos positivos de este gas, pero quizás sea mejor que les remita a una información más concreta y técnica, y por ello me permito recomendarles el libro de mi colega, la doctora Lourdes Vega, directora de I+D de Carburos Metálicos y manager global de tecnología, tratamiento de aguas y aplicaciones de CO2, y recientemente galardonada con el Premio Nacional de Física 2013: *El CO2 como recurso. De la captura a los usos industriales de forma didáctica y rigurosa*.

En este libro podrán disponer de una amplia documentación sobre las aplicaciones de este gas, que desde hace unas décadas ha sido encasillado en la categoría de "no deseable" pero que, como les decía al principio de este artículo, las cosas en el mundo científico no son tan categóricas, blancas o negras. Hay escalas de color donde un gas como el dióxido de carbono puede tener cabida y más en un mundo donde la ciencia trabaja en aportar soluciones de valor añadido a nuestra sociedad.

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Las cosas en el mundo científico no son tan categóricas, blancas o negras. Hay escalas de color donde un gas como el dióxido de carbono puede tener cabida y más en un mundo donde la ciencia trabaja en aportar soluciones

Europa ha logrado reducir las emisiones gases de efecto invernadero

04/06/2014

La Unión Europea ha logrado promover y aplicar la reducción de emisiones de gases a la atmósfera y parece que podrá alcanzar los objetivos planteados para 2020.



España ha logrado reducir un 7,5% de sus emisiones en 2012

Las emisiones de gases de efecto invernadero de la **Unión Europea** descendieron en 2012 y ya se encuentran en camino a la reducción planteada por el organismo para alcanzar en 2020. Así lo ha afirmado la **Agencia Europea del Medio Ambiente (EEA)**, que **anuncia un descenso de emisiones del 1,3% con respecto a 2013, y un 19,2% con respecto a 1990**. Los datos que corroboran la información ya fueron enviados a las Naciones Unidas. **Lee también**

» **Absorber todo el CO2 emitido requeriría una zona forestal equiparable a 3 Españas**

» **La contaminación ambiental genera 7 millones de muertes por año**

» **La UAH es la universidad española con el menor número de emisiones per cápita** Estos resultados logran poner a la Unión Europea a menos de 1% del porcentaje de reducción que el organismo se propuso alcanzar para 2020, afirmó la agencia. Los 15 primeros estados miembros de la UE son además firmantes del protocolo de Kioto, explica la EEA, que pretendía la reducción de 8% de las emisiones entre 2008 y 2012, y **estos países han logrado reducir una media de 11,8% de sus emisiones**. Las causas del descenso en las emisiones de gases de efecto invernadero En 2012 las emisiones descendieron, y esto se debió a 2 motivos, sostiene la EEA. Las reducciones en transporte e industria a causa de la crisis económica fue una de ellas, y la otra es **el creciente volumen de energía que se genera a través de fuentes renovables**. **El país que más ha reducido las emisiones netas en la UE ha sido Italia con el 45%**, ya que ha rebajado sustancialmente las emisiones en el transporte y la industria. A ésta le sigue Polonia, que ha logrado reducir el consumo de combustible fósiles, responsables de la mayoría de las emisiones. En el extremo opuesto, los países de la UE que más emitieron en 2012 fueron Alemania y Reino Unido, precisamente porque tienen una dependencia muy alta de combustibles sucios, que contaminan extremadamente el aire. Por su parte, **España se**

encuentra 4º en el listado de los que Estados miembros de la UE más han reducido sus emisiones, logrando recortarlas en 7,3%. La reducción de las emisiones y el crecimiento económico no son contrarias, sino que para que se complementen sin conflictos hace falta el éxito en las decisiones políticas. Es necesario continuar progresando, pero para ello **se necesita que las decisiones de los países sean a favor de una sociedad "baja en carbono y con seguridad energética"**, aseguró el director de la EEA, Hans Bruyninckx.

Fuente: El PaísAutor: Universia España

7 de febrero de 2014

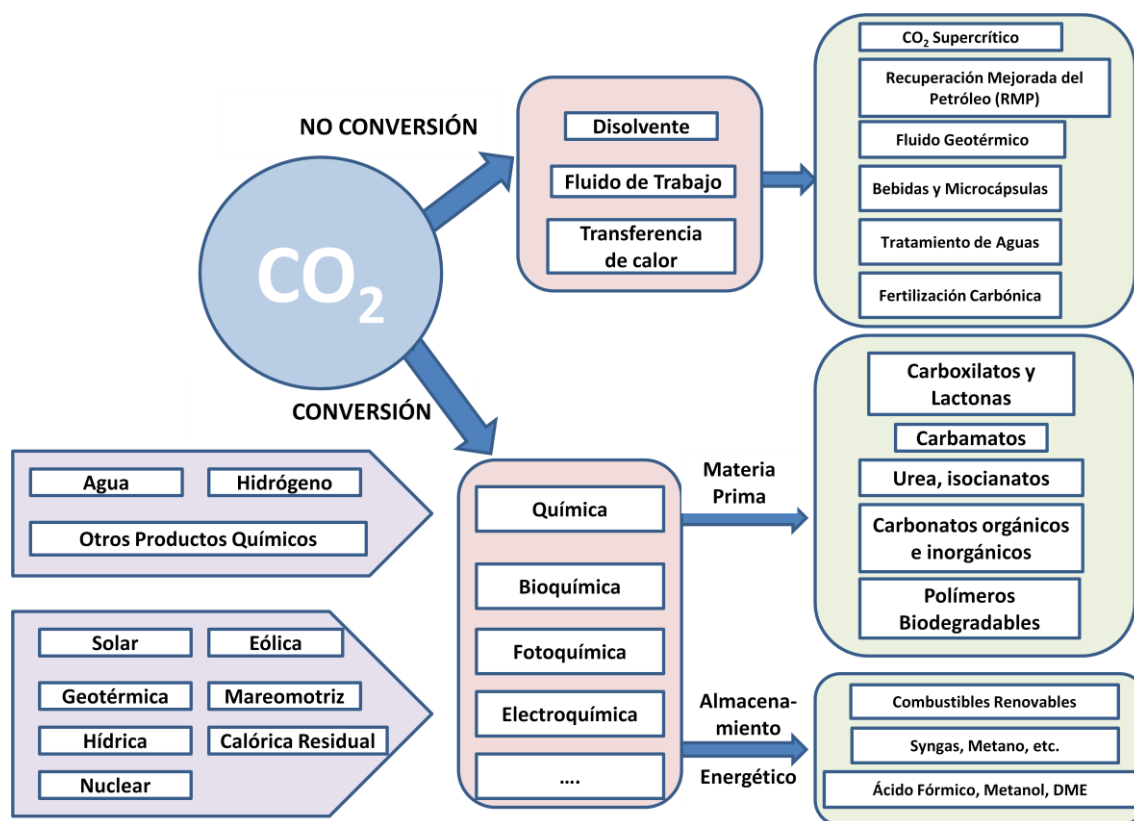
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CO₂ como materia prima

Objetivos del Grupo de Trabajo

Como consecuencia del debate climático, el CO₂ ha quedado estigmatizado como gas contaminante a los ojos de la opinión pública. El CO₂ no debe considerarse ni un contaminante ni un residuo, sino una fuente renovable que puede contribuir al desarrollo sostenible y a la mejora de la competitividad de la industria química. Existe la necesidad de cerrar el ciclo del carbono. La utilización del CO₂ puede ayudar a demostrar el potencial de la química como proveedor de soluciones a los grandes retos sociales tales como envejecimiento de la población, seguridad energética y cambio climático (por mencionar alguno).

El CO₂ como materia prima para la industria química puede ser utilizado de muchas maneras, tal como fuente renovable de energía y como ingrediente para desarrollar nuevos productos químicos, combustibles y/o polímeros (entre otros). Se están produciendo avances decisivos en la técnica de catálisis que hacen posible el aprovechamiento eficiente del CO₂ en procesos de producción sostenibles mediante tecnologías innovadoras. Actualmente se está fomentando la investigación de alternativas que permitan dar un uso positivo al CO₂ como materia prima en sustitución del petróleo. El siguiente paso, será conseguir que el CO₂ sea el compuesto que facilite la fotosíntesis artificial a través de procesos químicos.





Abre la primera gran central térmica de carbón con captura y almacenamiento de CO₂

Canadá acopla con éxito a una vieja central un sistema que evitará la emisión de un millón de toneladas anuales



En la imagen el extractor de dióxido de carbono

EVA M. RULL ■ MADRID

Una década después de que la empresa SaskPower empezará a investigar, y con la ayuda del gobierno de Canadá, se ha conseguido por primera vez aplicar la técnica de captura y almacenamiento de CO₂ a una instalación de generación eléctrica comercial, en concreto a una central térmica de carbón. Sin duda una gran noticia, entre otras cosas porque se han resuelto los problemas tecnológicos que limitaban el uso de la captura a los campos de explotación de gas natural y porque representa una oportunidad real para países que como Canadá o China, muy dependientes del uso de carbón en el mix energético.

Según informes de BP Statistical Review el uso de carbón cubrió en 2013 un 30 por ciento del consumo energético del planeta (su mejor dato desde los 70) y podría en 2016, siguiendo los datos de la Agencia Internacional de la Energía, llegar a desbancar al petróleo. Es evidente que este material está lejos de ser una fuente energética superada.

El Boundary Dam, que es como se llama la central, se encuentra al oeste del país y tiene una capacidad de 110 MW, con lo que es capaz de alimentar unos 110.000 hogares cada año. **Con el sistema que se ha instalado, se atrapa hasta un 90 por ciento de las emisiones, es decir un total de un millón de toneladas al año,** el equivalente, por tanto a retirar de la carretera unos 250.000 coches. Parte del CO₂ se utilizará en la recuperación mejorada de petróleo (se inyecta el gas en un campo de petróleo; ésta aumenta la presión y el líquido fluye con más facilidad) y parte quedará almacenado en las formaciones geológicas del subsuelo, a unos 3,4 km de profundidad.

El proceso que utiliza es el siguiente. El carbón se quema para producir electricidad y los gases que se generan se extraen por una chimenea hasta un reactor. En el interior de éste, hay una solución líquida que se llama amina, la cual es capaz de separar los diferentes gases y unirse al CO₂, formando una material casi líquido

que servirá para nuevos usos como la recuperación de petróleo o para su almacenamiento. En el caso de Boundary Dam se ha elegido un **área a 3,4 km de profundidad compuesta por piedra caliza y que ocupa una extensión de casi 25 campos de fútbol.** «Esta piedra caliza se encuentra bajo cuatro capas de piedra rocosa que sellan el depósito de gas. A esa profundidad y con el tiempo, el dióxido de carbono puede llegar a mineralizarse», explican fuentes de la empresa energética. El depósito está siendo monitorizado y ha sido estudiado para asegurar que no se producen microseísmos a causa de variaciones en la presión del terreno.

La utilización de aminas no es nueva. De hecho, se utiliza en las refinerías de gas natural desde finales de los 70, aunque sí es la primera vez que se aplica a una planta de producción de electricidad de tamaño comercial. Sin embargo, José Manuel Valverde de la Facultad de Físicas

La fórmula, aplicada hasta hoy en el refinado de gas natural, utiliza un compuesto líquido que atrapa las partículas por unos 70 dólares la tonelada

de la Universidad de Sevilla alerta «es un planta comercial pero es pequeña. Las que se construyen actualmente son diez veces más grandes». La importancia, por tanto, reside en que se trata de un piloto que demues-

tra la viabilidad de esta tecnología que por primera vez se aplica al carbón. «Una planta de 100 MW es suficiente para demostrar que la técnica es escalable a centrales de carbón de 300-500 MW. Parece que han solucionado los problemas técnicos puesto que la composición de los gases de una central térmica de carbón contienen altos niveles de nitrógeno, que hacen que se envenenen las aminas», explica Bernardo Llamas, ingeniero de Minas, profesor de la Universidad Politécnica de Madrid y miembro del grupo de captura y almacenamiento de CO₂

La empresa afirma que esta tecnología, que no sólo captura CO₂ sino otros gases como el dióxido de sulfuro, es escalable a cualquier otra planta del mundo, aunque uno de los problemas es el precio. Esta instalación ha costado **993 millones de euros.** «El uso de aminas requiere mucha energía porque necesita que se regenere el compuesto tras cada uno de los procesos», afirma Valverde. «Es bastante caro.



¿QUÉ SUCEDE EN ESPAÑA?

En 2010 España era pionera en la investigación y prueba de técnicas de captura. La Fundación Ciudad de la Energía instaló una caldera para ensayar la combustión de carbón con oxígeno en vez de con aire, para conseguir una corriente concentrada de CO₂ para su posterior almacenamiento. Otra de las plantas pioneras estaba en Elcogás en Puertollano (Ciudad Real). Fue la primera

planta piloto en el mundo en capturar una tonelada de CO₂ en 2010; ahora está en riesgo de cierre a 31 de diciembre de este mismo año. En Oviedo también se ensayó por primera vez con tecnología Ca-Looping, que utiliza cal para atrapar dióxido de carbono. A día de hoy España supera los objetivos de emisiones mientras que los proyectos parecen haber quedado en suspenso.

El coste por tonelada es de 70 euros», afirma Llamas. Mientras, el precio por emisión de CO₂ en Europa, es decir lo que les cuesta a las empresas emitir, oscila entre seis y diez euros. El futuro de esta tecnología y en general del almacenamiento parece ser positiva, ya que las emisiones de CO₂ no paran de crecer. Los científicos del Proyecto Global del Carbono alertan de que en 2014 se batirá un nuevo récord en la emisión, que alcanzará los 40.000 millones de toneladas. Esta cantidad limita las futuras emisiones a los 1,2 billones de toneladas, alertan los expertos, si no se quiere superar los dos grados centígrados de calentamiento climático. Un margen que a este ritmo se podría alcanzar en sólo 30 años. Además, estas emisiones proceden principalmente de la quema de combustibles. Llamas, quien acaba de volver del prestigioso congreso internacional «Greenhouse Gases Technology 12» explica: «Se percibe mucho interés en países como Estados Unidos, Australia, Canadá y Reino Unido. Sin duda, la siguiente generación de centrales llevarán incorporados estos sistemas de captura».

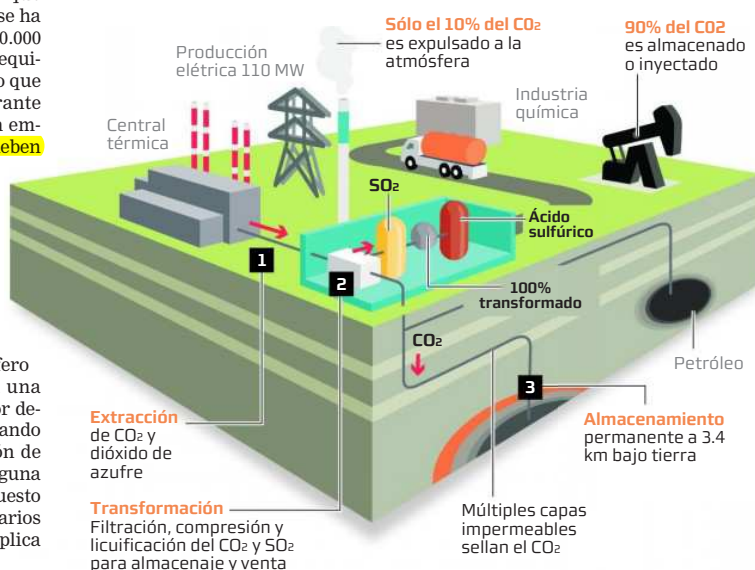
LUGARES DE ALMACENAMIENTO.

El precio de la tecnología también descenderá, entre otras cosas porque hay muchos grupos, como el de Valverde en España que investigan, entre otros, con el uso de cal en vez de las mencionadas aminas. La cal es el segundo material más abundante de la tierra y según las pruebas llevadas a cabo hasta ahora –se han experimentado en pilotos de 100 kW, incluso en Alemania ha habido una planta de un MW–, el precio de la captura con este materia prima podría bajar hasta los 14 euros por tonelada.

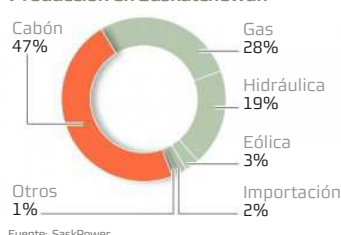
«El Panel Intergubernamental sobre el Cambio Climático ha estimado que formaciones rocosas como las que se ha utilizado pueden albergar hasta 10.000 gigatoneladas de CO₂, una cantidad equivalente a todo el dióxido de carbono que emitirá el hombre en la tierra durante 600 años», afirma la compañía. Sin embargo, «las estructuras geológicas deben ser adecuadas. Por ejemplo, en Europa hay mucho interés en el estudio de los acuíferos salinos a gran profundidad; acuíferos muy profundos que contienen muchas sales y que nunca podrían tener otro uso. Lo importante es que estén confinados, sean seguros y estables. El proyecto europeo Sleipner eligió un acuífero salino, llamado Utsira, situado a una profundidad de 800-1.000 metros por debajo del fondo marino. Está capturando desde 1996 a un ritmo de un millón de toneladas al año y no ha tenido ninguna incidencia en la presión del suelo, puesto que la extensión del depósito es de varios miles de kilómetros cuadrados», explica Llamas.

Capturar el dióxido de carbono para almacenarlo y uso irán de la mano. «Los muchos usos industriales que tiene nunca cubrirán el volumen de emisiones por lo que habrá que almacenar en depósitos», concluye Llamas. Es un poco lo que sucede en esta planta de Canadá, donde se captura y parte se usa para seguir extrayendo petróleo, con la diferencia de no se está explotando un yacimiento de dióxido de carbono como en otros casos sino que se está reciclando el gas que de otra forma se emitiría libremente.

CO₂ neutralizado y reciclado



Producción en Saskatchewan



Beneficios de la tecnología CCS*

(* Carbon Capture and Storage)



AC / LA RAZÓN

PLANETA TIERRA

RAMÓN TAMAMES

Catedrático de Estructura Económica / Cátedra Jean Monnet



Canta, carricerín

En un mundo lleno de avatares, de los que se resaltan mediáticamente los más morbosos, y cuando las pasiones se desatan en torno a disputas territoriales, religiosas, ideológicas, conflictos de intereses, etc., la noticia del retorno del minúsculo pájaro carricerín a España, cabe saludarla

como una especie de bendición del cielo.

Y en esto coincido con el espléndido artículo de Raúl del Pozo, en el diario «El Mundo», el pasado martes 14, porque el hecho de volver a un país después de diez años de ausencia, un ave tan delicada y elegante, es como un mensaje que a los amantes de la naturaleza nos alivia de penas y dificultades cotidianas.

Un ornitólogo de mi círculo de amistades me pone al corriente de que el carricerín común es un ave de la familia Silvidae, que habita en Eurasia y África, de colores pardos, con la espalda y las alas veteadas. Es un migrante esforzado de largos recorridos, desde las áreas nórdicas de su origen hasta el Sahara, volando siempre para

alcanzar esos alejados hábitats africanos.

Y además, por si fuera poco, es un insectívoro a carta cabal que contribuye a sanear los humedales donde la vida florece, como también lo hacen las miasmas más diversas que él ayuda a controlar.

En un país en el que el medio ambiente y la ecología son asignaturas aún por de-

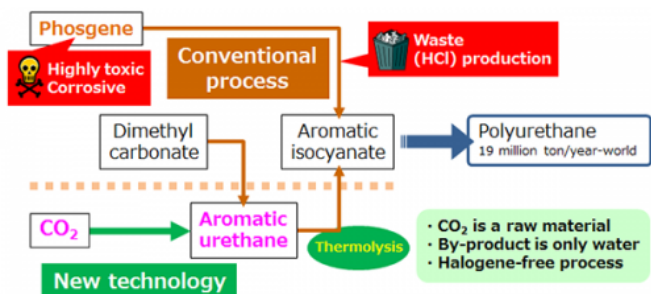
«Es un insectívoro a carta cabal que contribuye a sanear los humedales»

sarrollar en plenitud, el carricerín se asemeja a aquella paloma que con un ramo de olivo en su pico –luego idealizada al máximo por Picasso–, anunció el pacto entre Yavé y los hombres. Con la enseña de los ecologistas, ulteriormente, sustanciada en el arco iris; enunciándose así la paz de la naturaleza, por primera vez, y literariamente, en el Génesis, primer libro de la Biblia.

Bienvenido carricerín al Jardín de las Hespérides, hoy maltratado, deteriorado, con sus problemas y dificultades, con el estrés de tantos que no encuentran la forma de salir adelante en sus vidas. Tu llegada anuncia tal vez un nuevo tiempo de sonrisas más abiertas.

Efficient synthesis of polyurethane raw materials from carbon dioxide

25 November 2014



Conventional urethane manufacturing process and the developed aromatic urethane synthesis process

Japanese researchers have developed a new, high-yield reaction process to obtain aromatic urethane from carbon dioxide (CO₂), amine, and tin alkoxide. Aromatic urethane compounds are chemical substances currently used as drugs, agrochemicals, etc., but show high promise as raw materials for polyurethanes.

Currently, highly toxic and corrosive phosgene is used as the raw material for the manufacture of polyurethanes. In addition, a large amount of waste is produced in its manufacturing process and there was a strong demand for conversion to a manufacturing process that was more environmentally friendly.

AIST has been conducting development of an ideal, environmentally friendly urethane synthesis process that theoretically does not produce any waste, by using inexpensive and abundant CO₂, amine, and alcohol as its raw materials. However, technology developed until now was limited in the types of urethane it could synthesize, and aromatic urethane, the raw material for polyurethane could not be synthesized. In this study, it was discovered that aromatic urethanes can be synthesized with high yield when amine and tin alkoxide are reacted with high-pressure CO₂.

The details of this technology will be presented at

the 44th Petroleum-Petrochemical Symposium of JPI to be held at Asahikawa Grand Hotel (Asahikawa, Hokkaido) on October 16 to 18, 2014.

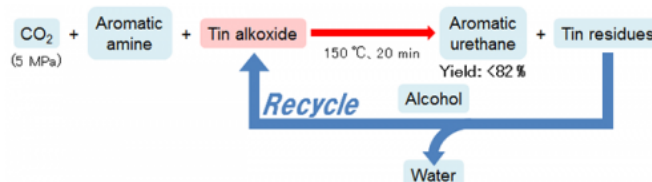


Figure 1 : Synthesis of aromatic urethane from CO₂, aromatic amine, and tin alkoxide

With the longing for a safe, secure, and affluent society, the importance of reducing hazardous substances and waste, improving energy efficiency, and converting to the use of recyclable resources as raw materials is increasing. It could be said that the supply of chemical products, materials, and components, based on "green and sustainable chemistry," is directly linked with sustained development of the chemical industry.

Polyurethane is a material widely used in daily living and building materials, automobile parts, paint, and other uses, and its annual global production reaches 19 million tons (2013). However, currently, a process using phosgene, a highly toxic and corrosive chemical that is a regulated substance under the Act on the Prohibition of Chemical Weapons and the Regulation of Specific Chemicals is used to synthesize raw materials for polyurethane. In addition, it also requires a large amount of chlorine. Because this synthesis process has many problems, there has been a strong demand for alternative synthesis processes that are environmentally friendly.

A process to thermally decompose urethane obtained from a reaction between amine and dimethyl carbonate is known to be a synthesis

> **NODOS / PLANETA RESPONSABLE**

- Carbuos Metálicos reutiliza el CO₂ de una vidriera para la industria
- CocaCola tiene un plan de devolución forestal del agua que gasta
- Preocupa reducir la huella de carbono de los equipos de frío

> **DIFERENTES**

Rafael Navarro



El mercado único real

En la cumbre económica de Davos cada año es más frecuente el debate sobre la tecnología, pero sin embargo sigue primando informativamente la difusión de la macroeconomía y las valoraciones políticas sobre la situación de los países.

En la edición de 2015 se ha hecho un paralelismo muy gráfico para comparar cómo de integrado estará internet en un futuro muy próximo en nuestras vidas. «Se borrará la barrera entre el mundo *online* y el *offline*», sentenció el presidente ejecutivo de Google, **Eric Schmidt**. «Internet será como el oxígeno», apostilló el director ejecutivo de Vodafone, **Vittorio Colao**.

Internet es realmente quien ha roto todas las barreras, en lo comercial, en lo intelectual y hasta en lo político; la nueva comunicación está en la base de la nueva política.

La revolución económica va a ser mucho más profunda de lo que nos imaginábamos la mayoría. Para el presidente y director ejecutivo de Cisco, **John T. Chambers** la digitalización absoluta hacia la que vamos provocará la desaparición del 40% de las empresas de hoy. «Primero hay que pensar en digital, después en el Internet de las Cosas y luego en la innovación rápida», destacó en Davos.

Y tan lejos como ayer vimos un ejemplo práctico en España. En la inauguración de la Feria Internacional del Turismo (Fitur) nos encontramos no sólo con que el mundo del comercio turístico ha transformado por completo ya a las agencias de viajes, sino también al resto de actores que te ofrecían rutas enlazadas que ahora se sirven enlazadas, o el wifi portátil para mantener la misma compañía fuera de casa.

Si a todo esto añadimos los avances para eliminar las barreras del idioma con los traductores simultáneos que están a un paso de ser instantáneos en tiempo real con cualquier *smartphone*, podemos decir ya que estamos entrando en el verdadero mercado único global, donde las barreras de los países van a ser ampliamente superadas en el ámbito del comercio.

Eso implicará cambios importantes en el pago de impuestos y en la legislación, por

Si van a desaparecer el 40% de las empresas, cuántos recursos se podría ahorrar la administración

eso es necesaria una implicación mucho más veloz de la administración en toda la era tecnológica. Y ahí surge una pregunta, si se cumple la predicción del director de Cisco de que desaparecerán el 40% de las empresas, ¿cuántos recursos de la administración no tendrán que suprimirse con las posibilidades que ofrece la nueva era?

Rafael Navarro es director de INNOVADORES.



Juan José Litrán, de CocaCola Iberia, en su conferencia durante el II Encuentro Planeta Sostenible. / ANTONIO MORENO

> **FORO**

La industria mira al planeta

Las empresas apuestan por la sostenibilidad como estrategia para ahorrar y crear nuevos vínculos con los consumidores. Por **Andrea Pelayo**

El primer edicto ambiental se dictó en Inglaterra hace cinco siglos, pero es ahora cuando el planeta ya no puede esperar más y, más allá de normativas, las propias empresas deben tomar la iniciativa. Lo tenían claro los ponentes de las segundas jornadas Planeta Responsable, organizadas por Objetivo Bienestar, donde se citaron compañías como CocaCola, Carbuos Metálicos (del grupo Air Products), H&M, Ecoembes, DKV o FCC, entre otras, para demostrar que la industria tiene mucho que decir en el camino hacia la sostenibilidad. Porque, como explicó Sara de Dios, fundadora y directora Global de Meaningful Brands, «cuanto más valor aportas en términos humanos y sostenibles, más valor generas».

Lo tenía difícil el representante de Carbuos Metálicos, Román Trías –director de relaciones institucionales y grandes cuentas de la compañía–. La empresa, que tiene 120 años de experiencia a sus espaldas, era seguramente la más desconoci-

da para el público general pero su capacidad de convertir el CO₂, «uno de los productos con peor prensa del mundo» según Trías, en un bien para la industria, dejó buen sabor de boca.

año– para tratarlo y utilizarlo a nivel industrial, especialmente en el ámbito alimentario.

Y de una compañía que produce, distribuye y vende gases para múltiples sectores como

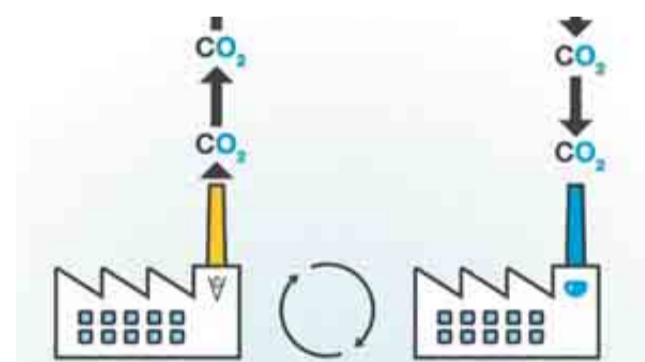


Gráfico de la colaboración de Carbuos Metálicos en Canarias.

«El problema del dióxido de carbono es si lo dejamos ir en la atmósfera y no le damos un uso», sostiene Trías. Su compañía ha llevado a cabo un proyecto pionero en su planta de Telde, en Gran Canaria, donde ha llegado a un acuerdo con una empresa vidriera vecina para capturar el CO₂ sobrante emitido por la chimenea de la vidriera –8.500 toneladas al

hace Carbuos Metálicos, a una que asume el reto de «seguir creciendo de un modo sostenible». Es el caso de CocaCola, que en su estrategia de sostenibilidad ha puesto como eje al agua. «Somos un 90% de agua y el resto de gracia», bromeó Juan José Litrán, director de relaciones corporativas de CocaCola Iberia, quien asegura que la compañía trata de «devolver

el 100% del agua que utiliza a la naturaleza». «Reducir y reciclar fue fácil pero reabastecer es más complicado», asegura el directivo.

Para conseguirlo, CocaCola ha lanzado el programa Plantando agua para la recuperación hidroforestal con la que ayudan a reabastecer en zonas como las Tablas de Daimiel –donde han conseguido devolver 500 millones de litros– o en los acuíferos de Castellón o el Tancat de la Pipa. «En estos años hemos devuelto el 52% de agua en 468 proyectos comunitarios en 100 países», recordó Litrán.

Pero no sólo el reabastecimiento es un reto para la marca internacional, que también se marca metas en la promoción de la agricultura sostenible. Otro compromiso adquirido es el de reducir la huella de carbono en un 25%. «Más que en los camiones, el reto está en los equipos de frío», advierte el directivo de CocaCola, quien afirma que desde 2004 han mejorado en un 19% la eficiencia energética en sus procesos de fabricación.

THE RAW MATERIAL CARBON DIOXIDE

A Dream Comes True

Crude oil is the raw material used to produce most plastics. What if one could conserve this limited resource and use carbon dioxide instead, which is available in abundance? For decades, chemists have considered this alternative a “dream reaction”, but now it is close to reality.





Experts at the CAT Catalytic Center of the RWTH Aachen University are supporting the work of researchers at Bayer Technology Services and Bayer MaterialScience and as such are making a major contribution to the success of the project.



“Nowadays, catalysis is the most important cross-functional technology in the chemical industry. It is used for the production of more than 85 percent of all products.”



Researcher Dr. Aurel Wolf, Bayer Technology Services

Carbon dioxide (CO₂) is considered the biggest polluter of all. However, if we are to believe the experts, this greenhouse gas will assume the role of a penitent in the near future and as a valuable raw material will ensure sustainable business development. CO₂ is to be integrated into the molecular structure of plastics and thus reduce the use of crude oil in the production of these indispensable engineering materials. With this development, specialists could pave the way for a meaningful use of this pollutant. And let us not forget that if less crude oil is consumed in production processes, the dependence of the chemical industry on this fossil raw material is also lowered. It is clearly a win-win strategy, also considering the fact that reserves of fossil raw materials are rapidly diminishing.

For this reason, scientists have long been searching throughout the world for alternatives that could replace crude oil altogether or only individual building blocks of the long molecular chains. But for decades this idea has only remained a theory because, in technical terms, the conversion of a chemical compound into a raw material for plastic synthesis is an enormous challenge. In the past numerous experts have all failed in their attempts to accomplish this conversion.

In contrast, researchers at Bayer Technology Services and Bayer MaterialScience have succeeded in taking a crucial step forward that could eventually make this dream become reality. One of these experts is Dr. Aurel Wolf, a chemist who is researching in the Reaction Engineering & Catalysis global competence center at Bayer Technology Services. “The basic problem is that carbon dioxide molecules are very stable and thus slow to react,” says Wolf and then adds a simple expla-

nation of this complicated scientific fact: “The carbon atom and the two oxygen atoms are tightly bonded to form CO₂. That makes it very difficult to integrate the inert trio into plastic molecules.”

What helps is activation energy, which allows chemical reactions with different partners. However, if the expenditure of energy is too big, the whole process becomes uneconomical. This has long been the case with carbon dioxide. As a consequence, chemists have always referred to a “dream reaction”, when it was a matter of processing the small molecule into syntheses. This reaction has now been successfully achieved with the help of catalyst research.

Catalysts can reduce the activation energy – and, as a result, make chemical processes more efficient. They can even make reactions feasible that would never possibly occur of their own accord. The use of CO₂ leads to a process under pressure, which is vastly different from conventional plastic production processes.

The experts at Bayer Technology Services know all about catalysts and reactions under pressure. They already began with the first experiments in 2005. Over the years, the collaboration with colleagues from Bayer MaterialScience was steadily intensified, as the Bayer Business Area is a potential customer for carbon dioxide. The chemical compound can be incorporated into polyols. The result are polyether polycarbonate polyols (PPP), which can serve as raw materials for the production of polyurethanes. These plastics are nearly universally applicable. They insulate buildings and refrigerators, ensure top-quality seating comfort and make cars lighter. In their search for a catalyst, the team did not have



Dr. Christoph Gürtler, Bayer MaterialScience

“The use of carbon dioxide as a raw material for polymers paved the way for a change of sources – away from fossil energy carriers to alternative sources.”

to start from zero. In 1969 Japanese researchers already showed that one can in principle activate CO₂ with a catalyst. “However, the speed of the reaction was extremely poor,” says Wolf. The advances in the following decades were rather modest. This changed radically in 2008, when the Bayer researchers succeeded in achieving the first important step on the way to the right process.

2009 then marked the beginning of a project supported by the German Federal Ministry for Education and Research (BMBF) and called “Dream Reactions”. The focuses of this project were the search for an improved catalyst and a better understanding of its principle mode of action. In addition to various other university partners, the CAT Catalytic Center of the RWTH Aachen University participated in the project, which Bayer Technology Services and Bayer MaterialScience managed together with the RWTH Aachen.

Just under a year later the project partners are already able to announce some first successes. This outcome is not only a small sensation for the participants, but also for professional circles. “In the meantime we have found catalysts that appear very promising,” says Wolf. The key to the success is the good teamwork with the colleagues from Bayer MaterialScience, “without this we never would have progressed so far so quickly”. He says this without the emotion usually attached to a sense of accomplishment. It was almost as if a fruit farmer remarks that the harvest was good: satisfied, but not at all euphoric.

Listening to Wolf, one would be more likely to gain the impression that it was mostly a matter of painstaking detective work. It was indeed very difficult to educe from him that it

was equally as much a question of resourcefulness and also of drafting the next, still better catalyst with the help of profound expertise in chemistry.

In the meantime Wolf and his team have tested some 200 different catalysts. For this work they have specially installed a reaction apparatus in their laboratory. Over and over again they brought together CO₂ and propylene oxide in this apparatus – each time with a different catalyst – and then heated the mixture. After a certain reaction time, they checked not only how much PPP was present, but also determined how much CO₂ was really incorporated in the polymer molecule at the end of the reaction. A maximum of 43 percent by weight is theoretically possible. At the beginning of the experiments the researchers were still far off from this goal and only managed to obtain a few percent; in the meantime, we have markedly cleared double-digits, says Wolf.

This good result heralded the start of the next step: the transition from the laboratory scale to technical scale production in a pilot plant. In May 2010 construction of this pilot plant began in the ChemPark Leverkusen, in which sample amounts of PPP were to be produced for project-internal testing. Not only Bayer Technology Services, Bayer Material Science and the CAT worked in close cooperation on this subsequent project, christened “Dream Production”; a further partner joined the team: RWE Power.

The biggest producer of electricity in Germany will provide the carbon dioxide for the planned “Dream Production”. It will be supplied from the lignite-fired power plant in Niederaussem. Here, the energy provider obtains gas in its Coal Innovation Center from flue gas in the first CO₂ scrub-



The new catalyst developed by Dr. Aurel Wolf and his team looks a lot like flour. With its help, it will be possible to use carbon dioxide as a raw material in plastics production.



Polyurethanes (PUR) are a class of materials that are particularly exceptional due to their diverse application possibilities. PUR foams are found in modern upholstered furniture (above) as well as in the soles of sport shoes.



“It is exceptional that in the field of CO₂ utilization, the entire value-added chain from the source to the final product is united in a single project. This offers enormous possibilities.”



Prof. Walter Leitner, RWTH Aachen

bing plant in Germany. And so the project now covers the entire value-added chain – from the raw material source (the flue gas cleaning) to the final product (polymers). As with the original “Dream Reaction” project, “Dream Production” will also be supported by the BMBF. Over a three-year period, the German Ministry will invest more than €4.5 million in the project.

With this new milestone, the role of Bayer Technology Services will also change. “The task of the first project was to search for a suitable catalyst and the right reaction control,” says Wolf. With the “Dream Production” the contribution of the technology service provider is quite different. Bayer Technology Services can now also offer its know-how in engineering and construction as well as in process design. For example, the company will contribute, among other things, the reactor and safety concept. “We feel that with Bayer Technology Services we have the right partner on board for this job,” says Dr. Christoph Gürtler, “Dream Production” Project Manager at Bayer MaterialScience. This shows once again how important the right partners are and intensive collaboration is for the success of an intricate new process.

If at the end it should prove to be possible to integrate carbon dioxide in a polyol like PPP and therefore in plastics like polyurethanes, two advantages are clearly evident: The carbon dioxide that is used will not be emitted into the atmosphere and crude oil as a raw material for polymer synthesis can be spared.

But the dream reaction can presumably allow still more. “An eco-efficiency analysis, which can quantify the total utility of a synthesis with a raw material like CO₂, should show

whether the entire process requires less energy overall than conventional polyol production,” says Professor Walter Leitner from the RWTH Aachen University.

And the work for the other project partner also continues. At Bayer MaterialScience researchers are currently investigating whether PPP may offer an additional benefit for polyurethanes and can perhaps even lead to improved product properties.

Aurel Wolf and his team are continuing to work on a further improvement of their catalysts. The aim is still to bring the portion of carbon dioxide in the PPP as close as possible to the maximum of 43 percent by weight. After all, one thing is absolutely clear: the higher this portion, the bigger the ecological benefits.

At present more than half a billion liters of crude oil are processed for the production of polymers – every day. This is a comparatively small share in total crude oil consumption, but every saving is welcome. And each carbon atom in a polymer that stems from carbon dioxide can save the raw material crude oil.

Besides this ecological benefit, the “Dream Production” project also offers the possibility to develop innovative products and thus to strengthen the added value of these sectors. If the “Dream Production” should one day be established throughout the industry and the separation of carbon dioxide from flue gas should become routine, then the white clouds typically billowing over coal-fueled power plants would be completely free of carbon dioxide. And then the next dream would certainly come true.

ARTICLE

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OPEN

Crystalline CO₂-based polycarbonates prepared from *racemic* catalyst through intramolecularly interlocked assembly

Ye Liu¹, Wei-Min Ren¹, Wei-Ping Zhang¹, Rong-Rong Zhao¹ & Xiao-Bing Lu¹

The crystalline stereocomplexed polycarbonates can be prepared by mixing enantiopure polymers with opposite configuration, which derived from the asymmetric copolymerization with CO₂ using enantiopure catalyst or/and chiral epoxides. Herein, we develop a powerful strategy for producing crystalline intramolecular stereocomplexed polycarbonates from *racemic* catalysts, which possess similar thermal stability and crystalline behaviour in comparison with the stereocomplexes by mixing opposite enantiopure polymers. Living polymer chains shuttle between catalyst molecules with different configurations to produce diastereomeric active species which is suggested to be responsible for the formation of isotactic multiblock polycarbonates in *racemic* bimetallic cobalt catalyst-mediated stereoselective copolymerization of CO₂ and *meso*-epoxides. Solid-state NMR spectroscopy study suggests that the interaction in the carbonyl and methine regions is responsible for the strong crystallization capacity and compact package structure in the crystalline polycarbonates.

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The alternating copolymerization of carbon dioxide (CO_2) with epoxides to provide degradable polycarbonates is widely regarded as a promising green process worthy of intense scrutiny since it utilizes CO_2 as C_1 feedstock, an abundant and renewable carbon resource^{1–6}. In the past decade, numerous homogeneous and heterogeneous catalyst systems were developed for this transformation for achieving enhanced activity and high molecular weight^{7–21}. Unfortunately, most of the previously reported CO_2 -based polycarbonates are amorphous, with a low glass transition temperature (T_g) $< 50^\circ\text{C}$, significantly confining their applications, especially as structural materials.

It is generally known that the physical properties of a polymer are determined not only by the monomer structure, its molecular weight and polydispersity, but also by the relative stereochemistry (the spatial arrangement of atoms or groups in a polymeric unit) of adjacent locations in the polymeric chains. A representative example is the widely studied polypropylene. The isotactic polypropylene is a typical semicrystalline material, possessing a melting temperature (T_m) of $130–175^\circ\text{C}$, dependent on the isotacticity, while the amorphous polypropylene is a viscous polymer at ambient temperature with a T_g of $\sim 0^\circ\text{C}$ (ref. 22). For CO_2 -based polycarbonates, in comparison with their amorphous structure, the crystalline forms should show improved thermal and mechanical properties, due to the high stereoregularity. In the recent contributions, some crystalline polycarbonates were prepared by stereospecific copolymerization of CO_2 and epoxides using enantiopure metal-complex catalysts^{23–25}. Notably, isotactic polycarbonates from *meso*-epoxides showed high levels of crystallinity, possessing T_m s of $179–273^\circ\text{C}$, dependent on the structure of the epoxides^{26–30}. Interestingly, the cocrystallization of amorphous isotactic polycarbonates having opposite configurations and identical structures was observed to form crystalline stereocomplexes^{31,32}, which show enhanced thermal stability and new crystalline behaviour, significantly distinct from the component enantiomers. These discoveries open up a new way to prepare various semicrystalline materials having a wide variety of physical properties. Nevertheless, these crystalline materials all originate from chiral

isotactic polycarbonates prepared by the enantiopure metal-complex-mediated CO_2 /epoxides copolymerization. As a consequence, these processes are far away from practical applications, due to the high cost of chiral catalysts. Therefore, the exploration of the synthesis of crystalline CO_2 -based polycarbonates from *racemic* catalyst and *rac*- or *meso*-epoxides is highly desirable.

Herein, we report an approach for the synthesis of intramolecular stereocomplexed polycarbonates by stereoselective copolymerization CO_2 with *meso*-epoxides using *racemic* dinuclear Co(III) complex as catalyst (Fig. 1), which possess similar thermal stability and crystalline behaviour in comparison with the stereocomplexes by mixing opposite enantiopure polymers.

Results

Synthesis of crystalline polycarbonates from 3,5-dioxaeptide.

For the alternating copolymerization of CO_2 with *meso*-epoxides mediated by *racemic* isotactic catalyst systems, three possible microstructures might be observed in the resultant copolymers, dependent on the copolymerization chain growth rate (R_g) and polymer chain-transfer rate (R_t) (Fig. 2). Only when R_g is significantly higher than R_t , the *racemic* isotactic catalyst-mediated copolymerization reaction provides isotactic polycarbonates or isotactic multiblock polymers. The *racemic*-(SalBinap)- AlO^iPr complex has been demonstrated to be very effective for the ring-opening polymerization of *racemic* lactide, affording the crystalline, stereoblock polymers³³. Coates and co-workers presented the first report for synthesizing a broad range of highly isotactic polyethers via the enantioselective polymerization of *racemic* epoxides using *racemic* catalyst^{34–36}. In this system, (*S*)-binaphthol linked dinuclear cobalt complex predominantly catalysed the ring-opening polymerization of (*S*)-epoxides to afford (*S*)-polyethers, while the polymerization of (*R*)-epoxides only concerned (*R*)-binaphthol linked catalyst to provide (*R*)-polyethers. The resultant mixture of (*S*)- and (*R*)-polyethers are highly isotactic, and most of them display high T_m values. Nevertheless, no cocrystallization occurs in the resultant mixture, in comparison with (*S*)- or (*R*)-polyethers.

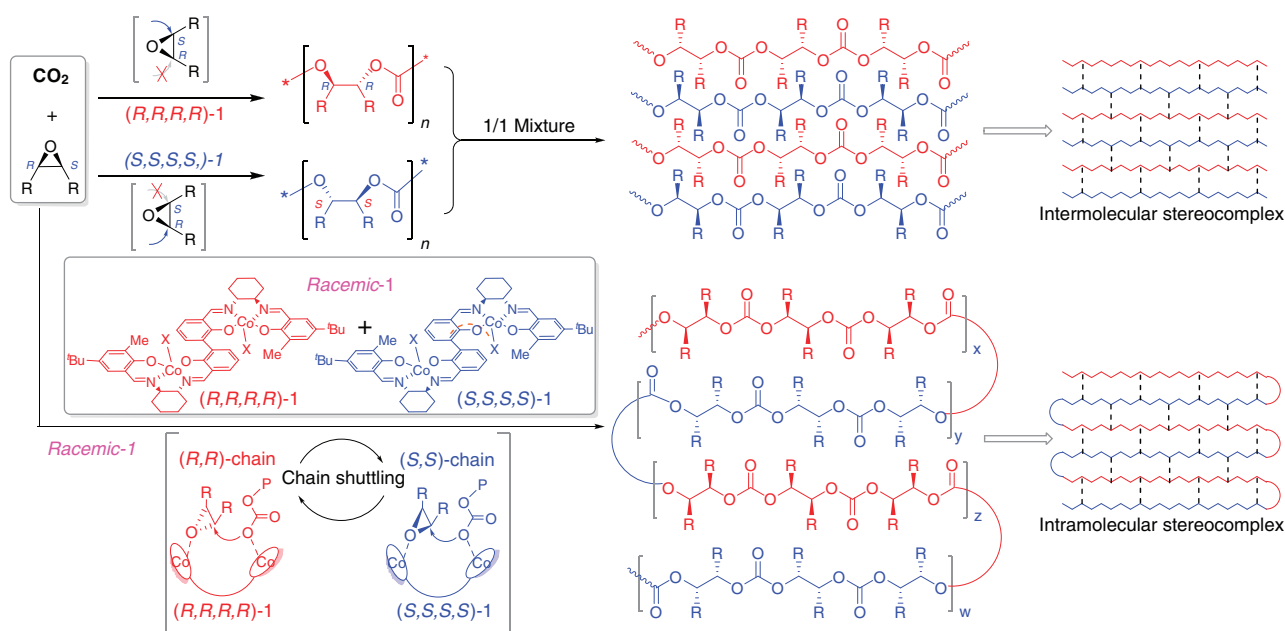


Figure 1 | Synthesis of stereocomplexed polycarbonates. The difference in the synthetic routes of intramolecular and intermolecular stereocomplexes from copolymerization of CO_2 with *meso*-epoxides.

Initially, *racemic* dinuclear Co(III) catalyst **1** was first applied to the alternating copolymerization of CO₂ with 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (CXO), a *meso*-epoxide with high reactivity. Previous study demonstrated that isotactic polycarbonates from CXO/CO₂ enantioselective copolymerization (PCXC) exhibited a melting temperature of 242 °C (ref. 28). Notably, when (R)-PCXC and (S)-PCXC are mixed in equivalent amounts, cocrystallization occurs, affording a stereocomplex with a new crystalline behaviour, significantly different from that of the sole configuration PCXC³². As a consequence, it was expected to form crystalline stereocomplex from *racemic* dinuclear Co(III) catalyst **1**-mediated CXO/CO₂ copolymerization, if (R,R,R,R)-**1** in the *racemic* catalyst system predominantly produces enantiopure (R)-PCXC, and (S,S,S,S)-**1** mainly affords enantiopure (S)-PCXC. We delightedly found that the CO₂/CXO copolymerization using *racemic-1* in conjunction with PPN-DNP (PPN, bis(triphenylphosphine)iminium; DNP, 2,4-dinitrophenoxide) at

25 °C and 1.5 MPa CO₂ pressure yielded highly crystalline polymer with a turnover frequency of 199 h⁻¹ (Table 1, entry 1). On the basis of fast-scan chip-calorimeter measurement (Flash DSC), high-melting endothermic peak was found at 340 °C, which is significantly different from the sole configuration (R)- or (S)-PCXC (Fig. 3, top, plots A and C). Also, the wide-angle X-ray diffraction study confirms its semicrystalline structure. Several diffraction peaks appearing at 2θ equal to 6.4°, 13.3°, 16.0°, 17.9°, 20.5° and 23.0° (*d* = 13.80, 6.65, 5.53, 4.95, 4.33 and 3.86, respectively) are consistent with the stereocomplexed PCXC by mixing enantiopure isotactic (R)- and (S)-PCXC in equivalent amount, but significantly distinct from that of the individual enantiomers (Fig. 3, bottom). Moreover, ¹³C NMR study demonstrates that no obvious difference was observed in the peaks corresponding to carbonyl and methine region between PCXCs prepared by mixing opposite enantiomers and by using *rac-1*, but significantly different from the atactic analogue (Fig. 4).

Previously, we have demonstrated that isotactic (R)-PCXC or (S)-PCXC were easily dissolved in various organic solvent, such as dimethylsulphoxide and tetrahydrofuran (THF), while stereocomplexed PCXC prepared from mixing equivalent (R)- and (S)-PCXC had no solubility in these solvents. It was found that the copolymer formed from the *racemic* catalyst system also had no solubility in both dimethylsulphoxide and THF, suggesting the formation of the stereocomplex. Furthermore, methanol was added as a chain-transfer reagent to the copolymerization mediated by *rac-1*/PPN-DNP catalyst system at the identical reaction conditions. We discovered that the resultant polymers were also crystallizable, although the melting temperature was decreased to a certain extent (Table 1, entries 1–4). For example, a *T*_m of 221 °C was found in the copolymer produced from *rac-1*/PPN-DNP catalyst system in the presence of 100 equivalents of MeOH, which is 119 °C lower than the PCXC resulted from the same catalyst in the absence of MeOH (Supplementary Fig. 1). The addition of methanol also resulted in the significant decrease in the copolymerization rate. In addition, a decrease in *M*_n is very obvious, and thereby causing

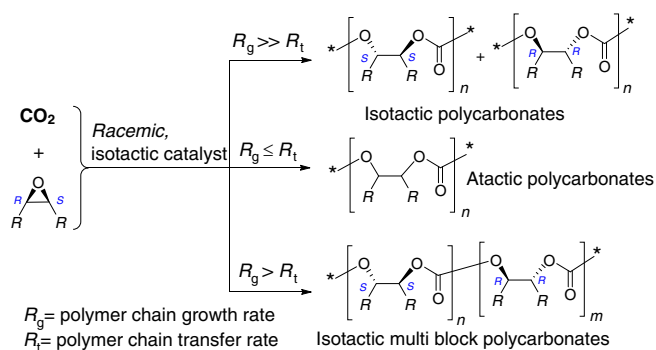


Figure 2 | Effects of polymer chain growth and transfer rate on the polymer structure. Three possible microstructures produced from the alternating copolymerization of CO₂ with *meso*-epoxides using *racemic* isotactic catalyst.

Table 1 | Enantiopure Co(III)-complex-mediated asymmetric CO₂/*meso*-epoxides copolymerization*.

Entry	Meso-epoxide	Cat./Co-cat./MeOH/epoxide [†]	Temp (°C)	Time (h)	TOF (h ⁻¹) [‡]	<i>M</i> _n (kg mol ⁻¹) [§]	PDI [§]	<i>P</i> _m	<i>T</i> _g / <i>T</i> _m (°C) [¶]
1		1/1/0/1,000	25	2	199	---	---	---	---/340 ^{††}
2		1/1/5/1,000	25	2	160	---	---	---	---/316 ^{††}
3		1/1/50/1,000	25	4	91	3.31	1.12	---	---/280 ^{††}
4		1/1/100/1,000	25	6	52	1.87	1.19	---	---/221 ^{††}
5		1/1/0/1,000	25	3	333	35.1	1.22	0.66	124/---
6		1/1/0/1,000	0	12	83	35.7	1.18	0.69	125/---
7 ^{‡‡}		1/1/0/1,000	25	8	124	32.0	1.26	0.82	125/---
8 ^{‡‡}		1/1/10/1,000	25	18	25	10.1	1.13	0.79	114/---

*The reaction was performed in neat *meso*-epoxides (3.0 ml), except entries 5–8 in toluene solution (epoxide/toluene = 1/2, volume ratio) in 20 ml autoclave and 1.5 MPa CO₂ pressure. *Racemic-1* was used as catalyst and PPN-DNP was used as cocatalyst. The polymer selectivity and carbonate linkage was >99% based on ¹H NMR spectroscopy.

[†]Molar ratio.

[‡]Turnover frequency (TOF) = mol of product (polycarbonates)/mol of catalyst per hour.

[§]Determined by gel permeation chromatography in THF, calibrated with polystyrene.

^{||}*P*_m was *m*-centred tetrads, determined by ¹³C NMR spectroscopy (CDCl₃, 125 MHz).

[¶]*T*_g and *T*_m were determined by DSC.

[#]The solubility of the polymer with high molecular weight and isotacticity was low in THF and DMF, so the *M*_n and PDI was not determined.

^{**}*P*_m cannot be determined by ¹³C NMR because the assignment of the polymer's microstructure has never been reported.

^{††}Determined by FSC.

^{‡‡}PPNPF₆ was used as the cocatalyst.

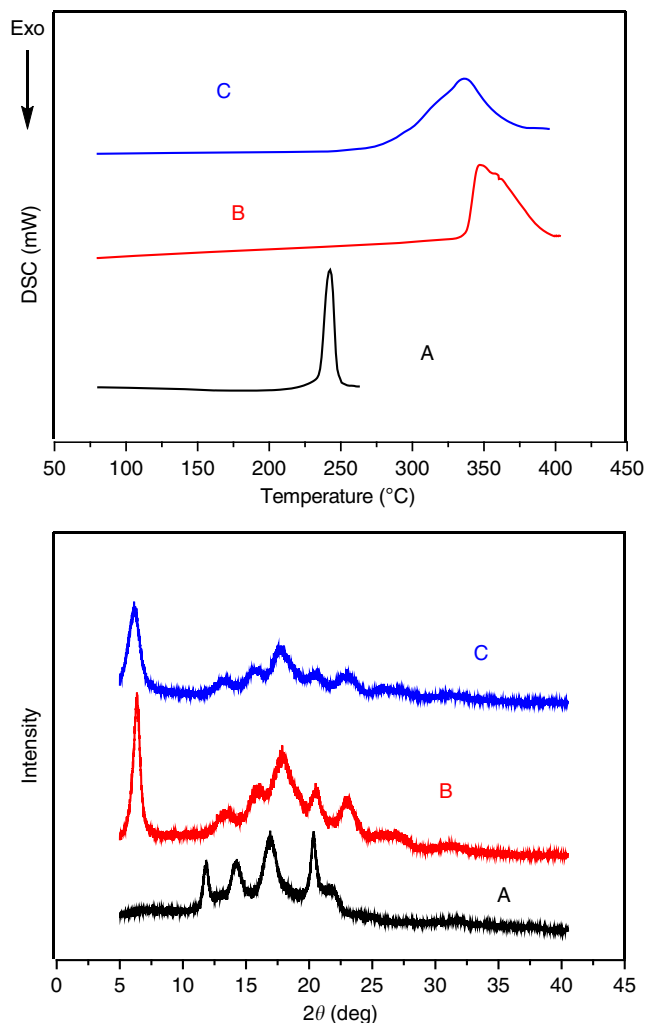


Figure 3 | DSC thermograms and wide-angle X-ray diffraction profiles of various PCXCs. (A) (*R*)- or (*S*)-PCXC with 99% ee; (B) stereocomplexed PCXC prepared by mixing (*R*)- and (*S*)-polymers with 1:1 mass ratio; (C) PCXC prepared from *rac*-1/PPN-DNP catalysed CXO/CO₂ copolymerization (Table 1, entry 1). The samples were crystallized isothermally at 180 °C for 2 h and samples of B and C in DSC thermograms was determined by FSC.

their dissolvable in THF and dimethylsulphoxide. ¹³C NMR analysis show that the peaks corresponding to carbonyl and methine region were found to be splitted when the reaction was carried out in the presence of methanol (Supplementary Fig. 2), suggesting a decrease in stereoregularity.

It is worth noting that the intensities of various diffraction peaks in the copolymer sample from *racemic* catalyst are obviously lower than the stereocomplexed PCXC obtained from the 1:1 mixture of the opposite enantiomers (Fig. 3, bottom, plots B and C). In addition, the melting endothermic peak is also slightly lower than that of the stereocomplexed PCXC with a *T_m* of 347 °C (Fig. 3, top, plots B and C). These results suggest that the crystallinity of the resultant PCXC from *racemic*-1 catalyst system is significantly lower than that of the stereocomplexed PCXC consisted of the mixed opposite enantiomers. We tentatively assume that the copolymer from *racemic*-1 catalyst system is an isotactic multiblock polymer. The reduced isotacticity originates from the stereoerrors in the copolymer caused by the polymer growth-chain transfer between (*R,R,R,R*)-1 and (*S,S,S,S*)-1 during the copolymerization. As a result, the intramolecular cocrystallization of the isotactic multiblock-PCXC

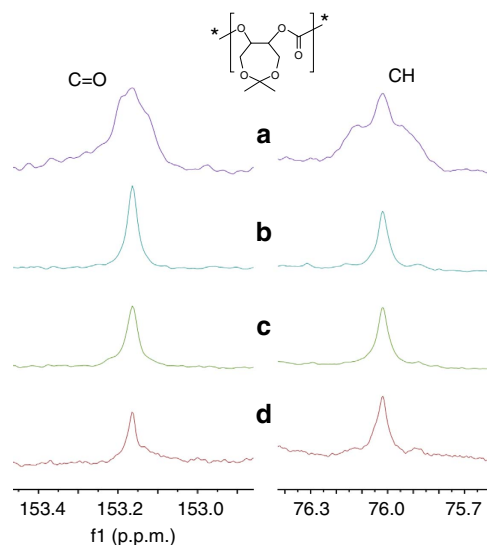


Figure 4 | The carbonyl and methine region of ¹³C NMR spectra of various PCXCs. (a) Atactic PCXC; (b) enantiopure isotactic (*S*)-PCXC; (c) stereocomplexed PCXC prepared by mixing (*R*)- and (*S*)-polymers in 1:1 mass ratio; (d) PCXC prepared from *rac*-1/PPN-DNP mediated CXO/CO₂ copolymerization (Table 1, entry 1).

from *racemic*-1 catalyst system predominantly contributes the formation of intramolecular stereocomplexed polycarbonates.

Solid state NMR spectroscopy is a powerful tool for studying the polymer segment, structure and dynamics. Macromolecular motions covering a wide range of time scales have long been considered to affect the physical and mechanical properties^{37–40}. Usually, polymers in amorphous state show high-amplitude motions, especially for the temperature above the *T_g*s. As previously mentioned, there are huge differences in physical properties for the amorphous, enantiopure and stereocomplexed-PCXCs in solid state, such as solubility, melting and crystalline behaviour. In the present study, solid state NMR spectroscopy was also employed for studying the difference in microstructure of various PCXCs (Fig. 5). Spin-lattice relaxation time (*T₁*) was measured for each carbon atom in four representative PCXC samples under the cross-polarisation condition by application of the saturation recovery-based sequence (Table 2). We discovered that the *T₁* value of carbonyl region for the enantiopure PCXC was longer than the amorphous state. Especially, the *T₁* value of carbonyl region for the stereocomplexed PCXC is up to 223 s, which is 175 s longer than the amorphous state and 131 s longer than enantiopure-PCXCs, in accordance with its much stronger crystallization capacity and compact package structure. Notably, it was demonstrated that PCXC resulted from *racemic*-1 (multiblock-PCXC) possessed a similar structure with the stereocomplexed PCXC, because its *T₁* value in carbonyl region also reached to 156 s. There is an interesting information for methine region, which was found to be splitted to three peaks for multiblock-PCXCs, and two peaks for stereocomplexed-PCXCs. The *T₁* values are 165 and 150 s for stereocomplexed-PCXCs, in agreement with 110 and 116 s for multiblock-PCXCs. However, no split was observed in the methine region for amorphous or enantiopure-PCXCs, in which *T₁* values are 38 and 36 s, respectively. Interestingly, *T₁* value for the middle peak in the methine region for multiblock-PCXCs is 50 s, corresponding to the methine region for amorphous or enantiopure-PCXCs. We tentatively ascribe it to the minor glassy state in the crystalline domains, which originated from the stereoerrors in the copolymer caused by the polymer growth-chain transfer

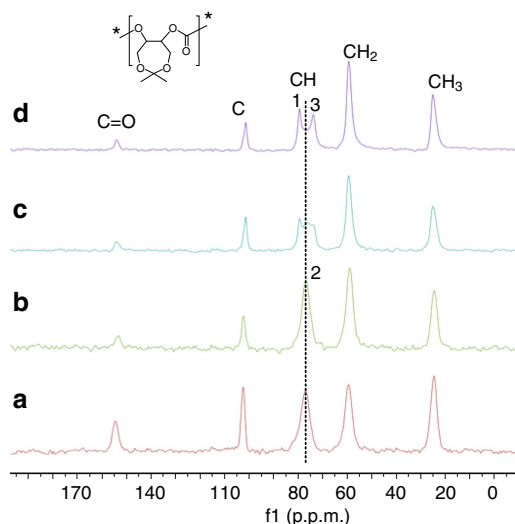


Figure 5 | ^{13}C CPMAS NMR spectra of various PCXCs. (a) amorphous-PCXC; **(b)** enantiopure (*S*)-PCXC; **(c)** isotactic multiblock-PCXC; **(d)** stereocomplexed-PCXC.

Table 2 | ^{13}C T_1 relaxation times for solid various PCXCs at ambient temperature*.

Entry	PCXC structure	T_1 (s)						
		C=O	C	CH	CH ₂	CH ₃		
				1	2	3		
1	Amorphous	48	21	—	38	—	26	1.3
2	(<i>S</i>)-enantiopure	92	29	—	36	—	21	1.6
3	Multiblock	156	40	110	50	116	58	1.3
4	Stereocomplexed	223	42	165	—	150	81	1.6

*Measured with CPMAS NMR using the saturation recovery-based sequence.

between (*R,R,R,R*)-**1** and (*S,S,S,S*)-**1** during the copolymerization. Nevertheless, T_1 values of quaternary and primary carbon for amorphous PCXCs were very similar to those measured for stereocomplexed- and multiblock-PCXCs, indicating that they are more inclined to motion and the energy can be released more easily.

Mechanistic study for *racemic-1* mediated copolymerization.

Indeed, ^{13}C NMR spectra of carbonyl and methine regions in Fig. 4 did not give the accurate isotacticity of the multiblock-PCXCs originated from the *racemic* catalyst system. In order to confirm the formation of the isotactic multiblock structure, cyclohexene oxide (CHO) was chosen as a model monomer of *meso*-epoxides for testing the stereoregularity of its CO_2 copolymer produced by *racemic* Co(III) complexes, since the microstructure of poly(cyclohexene carbonate) (PCHC) was well-characterized^{41–43}. Indeed, CHO also has relatively high reactivity in copolymerizing with CO_2 catalysed by both mono- and di-nuclear Co(III) complexes in the presence of a nucleophilic cocatalyst. In previous study, we have demonstrated that for the mono-nuclear Co(III) complex-mediated CO_2 /epoxide copolymerization, the dissociation of the propagating carboxylate from the metal centre is a much faster process than propagation, and the free propagating carboxylate can also act as a nucleophile for attack at a cobalt-coordinated

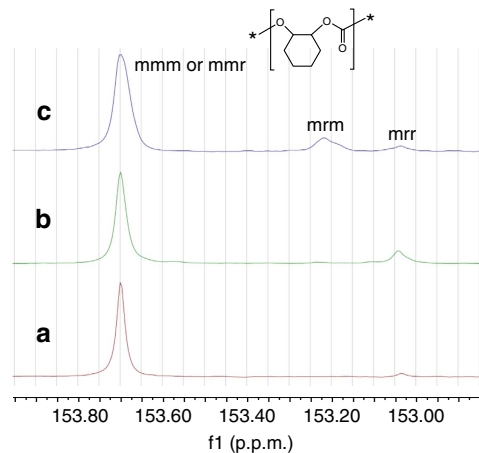


Figure 6 | Carbonyl region of the ^{13}C NMR spectra (125 MHz, CDCl_3) of various PCHCs. (a) PCHC with 0.96 P_m catalysed by enantiopure dinuclear Co(III) catalyst in toluene²⁷; **(b)** PCHC with 0.84 P_m catalysed by enantiopure dinuclear Co(III) catalyst²⁷; **(c)** PCHC with 0.82 P_m catalysed by catalyst *rac-1*/PPN-DNP (Table 1, entry 7).

epoxide, so the binary catalyst system of *racemic* mono-nuclear Co(III)–Salen complex and PPN-DNP for CHO/ CO_2 copolymerization provided atactic PCHC¹⁸. On the contrary, the *racemic* dinuclear Co(III) complex **1** gave isotactic-enriched PCHC, based on the ^{13}C NMR analysis. However, the isotacticity is obviously lower than that obtained from enantiopure dinuclear Co(III) complex. This means the occurrence of the copolymer-chain transfer between two kinds of catalyst molecules with different configurations.

Previously, various stereoregular PCHCs tetrad and triad sequences have been assigned in the ^{13}C NMR spectrum^{42,43}. In keeping with the previously established conventions in this field, it is important to note that [m] and [r] assignments used herein represent the relative stereochemistry of the carbons of the cyclohexene carbonate units (Supplementary Fig. 3). By synthesizing model poly(cyclohexene carbonate) oligomers or using Bernoullian statistical methods, all [mmm] and [mmr] tetrads were correlated to one central resonance at 153.7 p.p.m. and the remaining *r*-centred tetrads resided in the 153.3–153.0 p.p.m. range. The carbonyl region of the ^{13}C NMR spectra of various PCHCs resulted from different catalysts or conditions is shown in Fig. 6 (The relationship between the tetrad sequences and the polymer microstructures was described in Supplementary Fig. 3). On the basis of the peaks assigned to the appropriate tetrads in accordance with the literature, the PCHC with a P_m of 0.84 obtained from (*S,S,S,S*)-**1**/PPN-DNP catalyst system revealed a ^{13}C NMR spectrum with two distinct resonances at 153.70 and 153.04 p.p.m. assigning to [mmm + mmmr] and [mrr] tetrads, respectively (Fig. 6, plot B). Especially, the peak at 153.04 p.p.m. for PCHC with a P_m of 0.96 decreased significantly (Fig. 6, plot A). The *r*-centred [mrr] tetrad was produced by the errors in the chain growth (mismatched monomer was incorporated) and then corrected by the chiral environment that is constructed by the ligand around the metal centre through an enantiomorphic site control. However, for polycarbonates resulted from *racemic-1* (Fig. 6, plot C), a peak at 153.22 p.p.m. was discovered, corresponding to [mrm] tetrad, significantly distinct from PCHC resulted from (*S,S,S,S*)-**1** with the same P_m s (Fig. 6, plot B). Moreover, because of the formation of [mmr] tetrads, the peak corresponding to *m*-centred tetrads of polycarbonates resulted from *racemic-1* become broaden in comparison with the PCHC with the identical stereoregularity.

The ^{13}C NMR spectra of methylene region also confirmed the results (Supplementary Fig. 4). The presence of a small [mrr] peak also suggests that a minimal amount of the unpreferred enantiomer is incorporated into the chain at a level, consistent with the PCHCs described in plots A and B.

On the basis of [mrm] tetrad in ^{13}C NMR analysis, we can conclude that the polymer should have -RRRRRRSSSSSS- or -SSSSSSRRRRRR- sequences in the main chain. In fact, the polycarbonates produced from *racemic*-**1** has a stereo multiblock structure with alternating blocks of (*R*)- and (*S*)-polymer segments, rather than a stereocomplex of two highly enantiomerically enriched chains. A statistical model was used to simulate the spectrum of the PCHC with stereochemical defects formed in the polymer growth-chain transfer between (*R,R,R,R*)-**1** and (*S,S,S,S*)-**1**, suggesting that a block in the stereo multiblock PCHC contain an average of five enantiomerically pure carbonate units.

In the recent contributions, we demonstrated that the enantiopure biphenol-linked dinuclear Co(III) complex **1** was a privileged chiral catalysts for asymmetric copolymerization of CO_2 with various *meso*-epoxides, showing high activity and excellent enantioselectivity^{27–29}. The mechanistic study revealed that chain-growth step predominantly involves an intramolecular bimetallic cooperation mechanism, wherein alternating chain growth and dissociation of propagating carboxylate species takes turn between two Co(III) ions from the inside cleft of dinuclear Co(III) catalysts by the nucleophilic attack of the growing carboxylate species at one metal centre towards the activated epoxide at the other⁴⁴. It was also found that the propagating polymer chain transfer could be caused by protic solvents such as water and methanol, rather than the excess cocatalyst. Although every effort has been made to keep the copolymerization reaction anhydrous, we were concerned that trace quantities of water might be present, and thereby cause the growing polymer-chain transfer. Furthermore, it was found that the addition of 10 equiv. of methanol resulted in the significant decrease in copolymer molecular weight from 32.0 to 10.1 kg mol^{-1} , and a slight loss in P_m from 0.82 to 0.79 (Table 1, entry 8).

On the basis of the evidence and analysis mentioned above, the possible formation process for isotactic multiblock PCHC is proposed in the Fig. 7. Since the insertion of CO_2 into the growing polymer chain is a fast process, the predominant ring-opening event is the reactions of (*S*)-**1** with (*R*)-C–O and (*R*)-**1** with (*S*)-C–O bond of CHO, affording (*S*)-PCHC and (*R*)-PCHC, respectively (enantiomeric active species A and B). However, the adventours water or the addition of protic solvent probably results in polymer-chain exchange between the (*R*)-PCHC anchored on (*R*)-**1** and the (*S*)-PCHC anchored on (*S*)-**1**, affording the (*S*)-PCHC anchored on (*R*)-**1** and the (*R*)-PCHC anchored on (*S*)-**1** (diastereomeric active species C and D). At this point, polymer chain propagation resumes with the favoured stereoisomer, creating a diblock structure. The polymer chain exchange and propagation take place repeatedly to provide the isotactic multiblock polycarbonates.

It is a pity that the isotactic multiblock PCHC with a P_m of 0.82 was amorphous material with a T_g of 125 °C, slightly higher than the atactic PCHC. Indeed, no crystallizability of the isotacticity-enriched PCHC is not strange. In previous contribution, we have demonstrated that only PCHCs with more than 90% isotacticity were crystallizable²⁶. However, we expect with great passion the formation of the intramolecular stereocomplexed PCHC, since a stereocomplex formed by the polymer assembly of optically active PCHCs with opposite configurations was previously confirmed³⁰. In order to validate our supposition, solid state NMR spectroscopy was also employed for studying the difference of the microstructure of various PCHCs. (Supplementary Fig. 5 and

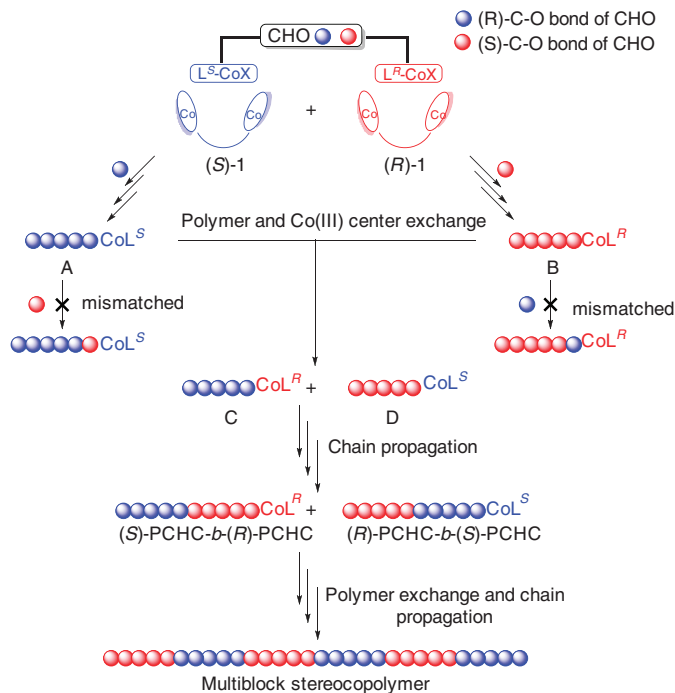


Figure 7 | Possible mechanism for the formation of isotactic multiblock polycarbonates. *Racemic* dinuclear Co(III) mediated CHO/ CO_2 copolymerization was selected as a model reaction.

Supplementary Table 1). As anticipated, the T_1 value of carbonyl region for the stereocomplexed PCHC is up to 271 s, which is 223 s longer than that for the amorphous PCHC. Similarly, the T_1 values of methine (250 and 195 s) and methylene carbons (146 and 110 s) for the stereocomplexed PCHC are significantly longer than that for the amorphous PCHC (35 s for methine region, and 23 and 21 s for methylene carbons). However, for the isotactic multiblock PCHC, the T_1 values of carbonyl region and methine carbons are 56 and 39 s, respectively, while that of methylene carbons are 26 and 24 s. These values are slightly higher than that for the amorphous state, but significantly lower than that for the stereocomplexed PCHC.

Discussion

In conclusion, novel intramolecular stereocomplexed polycarbonates were synthesized by the stereoselective copolymerization of CO_2 and *meso*-epoxides using *racemic* bimetallic cobalt catalyst system. Highly enantioselective chain growth in an enantiopure catalyst molecule and the copolymer-chain transfer between different configuration catalyst molecules results in the formation of the isotactic multiblock polycarbonates. Solid state NMR spectroscopy study suggests that the interaction in the carbonyl region is responsible for the strong crystallization capacity and compact package structure in the crystalline polycarbonates. This is the only example for the synthesis of crystalline CO_2 polymers from *racemic* catalyst. Due to the use of the inexpensive *racemic* or achiral ligand, the present synthesis strategy is of great importance for preparing various intramolecular stereocomplexed polycarbonates with enhanced thermal stability.

Methods

General. All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. CO_2 (99.995%) was purchased from Dalian Institute of Special Gases and used as received. Methylene chloride and chloroform were distilled from calcium hydride under nitrogen. Tetrahydrofuran and toluene were distilled from sodium/

benzophenone under nitrogen. Epoxides were purchased from Acros and distilled over calcium hydride.

Fast-scan chip calorimeter. Fast-scan chip calorimetry (FSC) was performed with the commercialized FSC (Flash DSC1, Mettler-Toledo, Switzerland). The empty chip-sensor was calibrated according to the standard procedure before the experiment. The ready temperature of test module for all measurements was set as 30 °C. Purge nitrogen gas was used as the protection atmosphere with the constant flow rate 50 ml min⁻¹. First cycle: from 20 °C to 280 °C at a heating rate of 3,000 K s⁻¹, and holding at 280 °C for 5 min, and from 280 to 20 °C at a cooling rate of 3,000 K s⁻¹. Second cycle: from 20 °C to 400 °C at a heating rate of 3,000 K s⁻¹. For all FSC analysis, the result was given based on second cycle.

Solid state NMR experiments. Solid state NMR experiments were performed using an Agilent DD2-500 MHz NMR spectrometer in 4-mm ZrO₂ rotors at MAS frequencies ranging from 12 to 14 kHz. ¹³C cross-polarisation MAS NMR spectra were collected at 125 MHz with a B1(¹³C) field nutation frequency of 100 kHz, a contact time of 3 ms and a recycle delay of 4 s. ¹³C spin-lattice relaxation experiments were carried out under CPMAS conditions using the saturation recovery-based sequence. The chemical shifts were referenced to the adamantane with the upfield methine peak at 29.5 p.p.m.

Details of other experiments see Supplementary Methods.

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Author contributions

Y.L. performed catalytic experiments, measurements, the copolymer characterization and mechanistic study. W.-M.R. participated in discussions and contributed important suggestions. W.-P.Z. and R.-R.Z. performed the solid state NMR analysis. X.-B.L. designed the research and conducted the experiments. X.-B.L. and Y.L. co-wrote the manuscript.

Additional information

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