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NOVEL RUBBERS PRODUCED FROM CO2-BASED POLYCARBONATES

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PURPOSE OF THE ABSTRACT

Nowadays, the fixation of carbon dioxide (CO2) into valuable products attracts increasing attention, since CO2 is an extremely abundant, non-toxic, inexpensive, and renewable feedstock.[1][2] Moreover, the design of climate-neutral processes is of paramount importance due to the increasing concerns about CO2 atmospheric concentration and its relation to global warming.[3] For these reasons, the idea of producing rubbers with a polycarbonate structure, taking advantage of the atom-efficient reaction of CO2 with epoxides (Figure 1), is an appealing goal.[4]

Due to its air and moisture stability, an aluminium amino-tris(phenolate) complex paired with bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) was chosen as homogeneous, binary catalytic system for the aforementioned reaction (Figure 1).[5] Under moderate heating and supercritical carbon dioxide pressure (45°C and 80bar, respectively), a wide range of epoxides with long alkyl chains were efficiently coupled with CO2 to give polycarbonates in good yields. Low temperatures and high CO2 pressures were chosen to inhibit the formation of cyclic carbonates and ether linkages, which are the possible by-products of the reaction (Figure 1).[6]

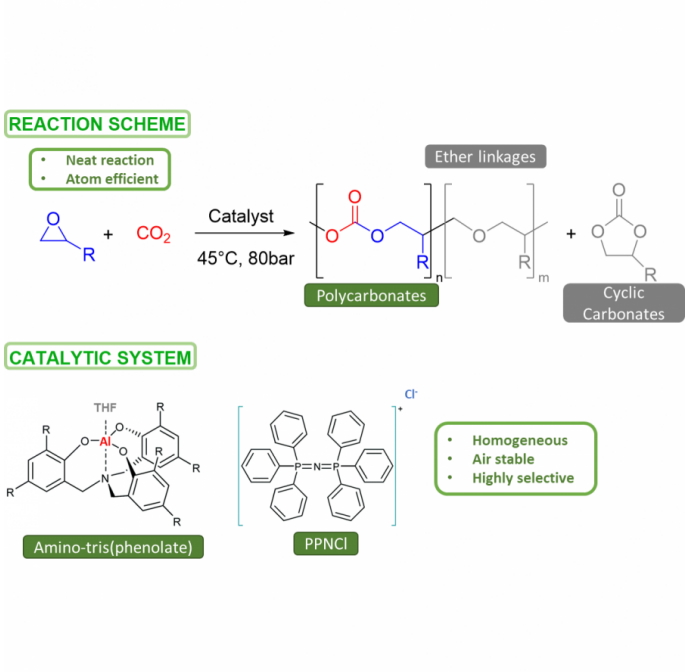
The chemical composition of the so-synthesised polycarbonates was characterised using FT-IR and both proton and carbon nuclear magnetic resonance (1H-NMR and 13C-NMR). The glass transition temperature (Tg) and the molecular weight distribution of the CO2-based polymers were determined through differential scanning calorimetry (DSC) and gel permeation chromatography (GPC), respectively. The Tg of the resulting polycarbonates is dependent on the length of the alkyl side chain and, thus, can be adjusted to values below room temperature.

The addition of allyl glycidyl ether (AGE) to the reaction mixture led to a terpolymerisation, which was achieved with almost complete conversion and very high selectivity towards the desired polycarbonate product.

Since the prepared polycarbonates contain pending vinyl groups derived from AGE, post-polymerisation modification was possible (Figure 2). Peroxide curing by reaction with dicumyl peroxide was attempted in order to yield rubbers. The crosslinked polycarbonates, which underwent gel-content test, showed a substantial change in their structure by passing from the liquid phase of the polymeric materials to the solid phase after cross linking (Figure 2). Moreover, they also displayed elastic deformation features, typical of rubber-like materials.

The efficient terpolymerisation of long-chained epoxides, AGE, and CO2 and the successful crosslinking of these polycarbonates to produce elastic rubbers open up a new range of applications of these CO2-based, green polymers.

FIGURES



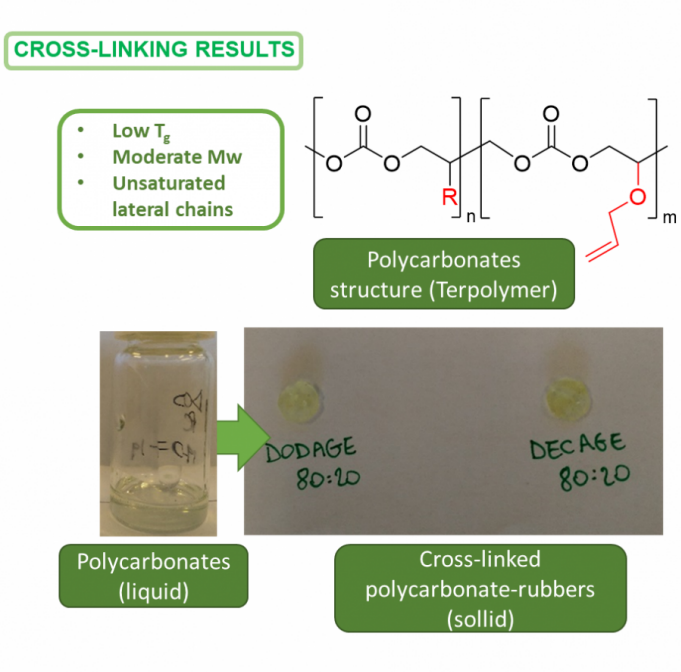


FIGURE 1

Reaction scheme and catalyst

At the top: atom-efficient coupling of epoxides with CO2 towards polycarbonates. Ether linkages and cyclic carbonates (in gray) are considered by-products.

At the bottom: binary homogeneous catalyst composed by PPNCl and Al amino-tris(phenolate) complex.

FIGURE 2

Peroxide curing results

At the top: structure of typical terpolymers that underwent peroxidic curing.

At the bottom: achievement of cross-linked polycarbonate-rubbers (solid) from liquid polycarbonates.

KEYWORDS

Polycarbonates | Rubbers | Green polymers | Carbon dioxide fixation

BIBLIOGRAPHY