



- (51) **International Patent Classification:** Not classified
- (21) **International Application Number:**
PCT/KR2015/013331
- (22) **International Filing Date:**
7 December 2015 (07.12.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
62/088,751 8 December 2014 (08.12.2014) US
62/199,983 1 August 2015 (01.08.2015) US
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- (81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,

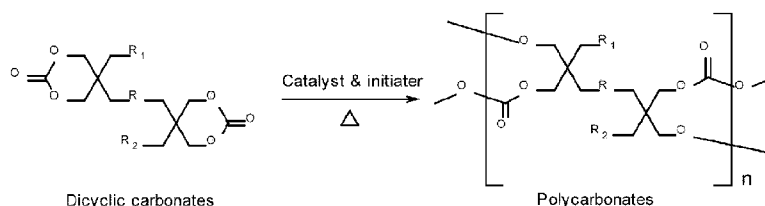
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BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
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MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished
upon receipt of that report (Rule 48.2(g))*

(54) **Title:** ALIPHATIC POLYCARBONATES AND PRODUCTION METHODS FROM CYCLIC CARBONATES THEREOF



(57) **Abstract:** Aliphatic polycarbonates are prepared by ring opening polymerization of six-membered cyclic carbonates or various ratio of mixtures of six-membered cyclic carbonates using catalysts. The resulting materials are further polymerized using the extra functional group such as additional 2nd cyclic carbonate, (meth)acrylate and allylate. This process and material(s) obtained provide chlorine (e.g. phosgene and chloroformate)-free and bisphenol-free polycarbonates and their derivatives for environment-friendly applications.

Description

Title of Invention: ALIPHATIC POLYCARBONATES AND PRODUCTION METHODS FROM CYCLIC CARBONATES THEREOF

Technical Field

- [1] This invention relates to carbonate building blocks, chlorine- and bisphenol-free polycarbonates, their derivatives prepared from six-membered functional cyclic carbonates. The invention further relates to production process of said building blocks and polymers, and use of those materials for different applications, e.g. plastics, resin, coatings, forms, biomedical, and biomaterial applications.

Background Art

- [2] Polycarbonates have been used for a wide range of applications from automotive parts to electronic appliances, and are obtained from aromatic or aliphatic dioxy compounds by means of a carbonate. The main polycarbonate material is obtained from polymerization of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) with toxic phosgene or diphenylcarbonate, which is derived from reaction of phenol with phosgene, and the product requires high purity without the presence of chlorinated impurities [1].
- [3] However, the main raw material, BPA shows estrogenic properties, and the release of BPA from polycarbonates has been studied on exposure and risk assessments in a large number of studies, because of the widespread use of polycarbonates in food and drink packaging, as lacquers to coat metal products such as food cans, bottle caps, water supply pipes, and dental sealants and tooth coatings (reviewed in [2]).
- [4] Aliphatic polycarbonates have been less interesting compared to aromatic polycarbonates because of their poor thermal stability and easy hydrolysis. However, since the last decade, aliphatic polycarbonates have been attracting attention due to increasing awareness of risks of BPA exposure from aromatic polycarbonates, and also for their unique combination of biodegradability and biocompatibility for medical applications. Aliphatic polycarbonates can be prepared mainly by 3 reaction pathways [3]. Aliphatic carbonates were prepared by polymerization of CO₂ with an epoxide (propylene oxide and ethylene oxide) using highly efficient catalysts. These amorphous polymers are currently in the early stage of commercialization. The condensation polymerization of aliphatic diols with dimethyl carbonate produced high molecular weight aliphatic polycarbonates using a catalyst (NaH) by two stage reaction consisting of oligomerization and polymerization at over 180°C. Aliphatic polycarbonates can also be obtained via ring opening polymerization (ROP) of their re-

spective cyclic monomers using different kinds of initiators and catalysts according to cationic, anionic, coordination, and enzymatic mechanisms, or metallic compounds as catalysts, which allow full control over molecular parameters along with chain-end group fidelity (reviewed in [4]). The ROP of cyclic trimethylene carbonate and its derivatives could also produce high-molecular-weight poly-(trimethylene carbonate), also as amorphous form ($T_g = 19^\circ\text{C}$). Cyclic carbonates used for preparation of aliphatic polycarbonates by ROP were reviewed, but were only mono-cyclic carbonates with limited functional groups [5].

- [5] Five-membered alkylene carbonates have been considered to a less extent for commercial use owing to thermodynamic properties in the ROP, while six-membered cyclic carbonates provide more opportunities to be used in the polymerization. The ROP of five-membered cyclic carbonates is a slow reaction that has been reported to proceed in the presence of catalysts such as metal alkoxides, metal acetylacetonates, and metal alkyls. The polymerization involves partial decarboxylation and the loss of CO_2 such that the polymer produced contains both carbonate and ether linkages. Therefore, six-membered cyclic carbonates are thermodynamically more suitable precursors, however their production has not been straightforward, and the monomers are not commercially available. Moreover six-membered cyclic carbonates functionalized with reactive groups such as 2nd cyclic carbonate of dicyclic carbonate, (meth)acrylate and allylate, which can be used in polymerization, have been limited in the preparation and polymerization. Although several examples of synthesis of bis- (five and six-membered) cyclic carbonates by complicated processes are known, the materials were only used to study urethane bond formation with diamines [6].
- [6] As interesting monomers, six-membered dicyclic carbonates, di-trimethylolpropane dicyclic carbonate and di-trimethylolethane dicyclic carbonate can be polymerized to polycarbonates. Di-trimethylolpropane dicyclic carbonate has been prepared from di-trimethylolpropane with phosgene, chlorocarbonates, dialkylcarbonates and diarylcarbonates using strong base catalysts by a two-step process comprising polymerization and depolymerisation at 250°C under 0.01 mbar [7]. The essential point in polymerization step was that the reaction leads to a soluble product and not to an insoluble, strongly crosslinked polymer. Therefore this indicated that the process was to prepare the cyclic carbonate, and the intermediate was an oligomer or low molecular prepolymer rather than polycarbonate. Also no specification and properties of the polymer were provided.
- [7] We have recently developed a facile process for production of various functional six-membered mono- and di-cyclic carbonates [8]. Allylated trimethylolpropane cyclic carbonate, (meth)acrylated trimethylolpropane cyclic carbonate can be polymerized to polycarbonate through the cyclic carbonate, and then the resulting polycarbonates can

be further polymerized with active groups of allyl and (meth)acryl groups by UV or thermal reaction in the presence of an initiator. Allyl group reacts with thiol group by the thiol-ene reaction mechanism by UV or thermal reaction. Acrylate and methacrylate are common monomers in polymer plastics, forming the corresponding polymers because the α,β -unsaturated double bonds are very reactive. Resulting polymers can be used as plastic, sheet or resin for conventional purpose, and biomedical and biomaterial applications of polycarbonate and polycarbonate copolymers.

- [8] Therefore the resulting polymers can be novel materials having unique properties and structures, and the production process provides a mild environment-friendly process without using phosgene, other chlorinated materials, and bisphenol.

Disclosure of Invention

Technical Problem

- [9] Although polycarbonates have been used for a wide range of applications from automotive parts to electronic appliances, and are obtained from aromatic or aliphatic dioxy compounds by means of a carbonate, since the main raw material, BPA shows estrogenic properties, thus the release of BPA from polycarbonates has been studied on exposure and risk assessments in a large number of studies, because of the widespread use of polycarbonates in food and drink packaging, as lacquers to coat metal products such as food cans, bottle caps, water supply pipes, and dental sealants and tooth coatings.

Solution to Problem

- [10] Accordingly, the present invention provides a process for ROP of dicyclic carbonate, e.g. di-trimethylolpropane dicyclic carbonate (diTMP diCC) and di-trimethylolethane dicyclic carbonate (diTME diCC) to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [11] Further, the present invention provides a polycarbonate prepared from dicyclic carbonate, e.g. diTMP diCC and diTME diCC by ROP in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [12] Further, the present invention provides a process for ROP of allylated cyclic carbonate, e.g. TMPME CC and TME ME CC to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [13] Further, the present invention provides a polycarbonate prepared from allylated cyclic carbonate, e.g. TMPME CC and TME ME CC by ROP in presence of catalyst at

ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.

- [14] Further, the present invention provides a process for cross linking of polycarbonate prepared from allylated cyclic carbonate, e.g. TMPME CC and TMEME CC to cross linked polycarbonate through thermal reaction of polycarbonate with thiol compound in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction with thiol compound in presence of initiator.
- [15] Further, the present invention provides cross linked polycarbonate prepared through polycarbonate prepared from allylated cyclic carbonate, e.g. TMPME CC and TMEME CC through thermal reaction of polycarbonate with thiol compound in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction of polycarbonate with thiol compound in presence of initiator.
- [16] Further, the present invention provides a process for thermal reaction of allylated cyclic carbonate, e.g. TMPME CC and TMEME CC with thiol compound to prepolymer in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [17] Further, the present invention provides prepolymer prepared through thermal reaction of allylated cyclic carbonate, e.g. TMPME CC and TMEME CC with thiol compound in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or with thiol compound by UV reaction in presence of initiator.
- [18] Further, the present invention provides a process for direct (one-pot) preparation of cross linked polycarbonate from reaction of allylated cyclic carbonate, e.g. TMPME CC and TMEME CC with thiol compound in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [19] Further, the present invention provides a process for ROP of (meth)acrylated cyclic carbonate, e.g. TMPmMA CC, TMEmMA CC, TMPmA CC and TMEmA CC to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [20] Further, the present invention provides a polycarbonate prepared from (meth)acrylated cyclic carbonate, e.g. TMPmMA CC, TMEmMA CC, TMPmA CC and TMEmA CC by ROP in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [21] Further, the present invention provides a process for cross linking of polycarbonate

prepared from (meth)acrylated cyclic carbonate, e.g. TMPmMA CC, TMEmMA CC, TMPmA CC and TMEmA CC to cross linked polycarbonate through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.

[22] Further, the present invention provides cross linked polycarbonate prepared through polycarbonate prepared from (meth)acrylated cyclic carbonate, e.g. TMPmMA CC, TMEmMA CC, TMPmA CC and TMEmA CC through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.

[23] Further, the present invention provides a process for ROP of mixture of (functional) cyclic carbonates to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.

[24] Further, the present invention provides polycarbonates prepared from mixture of (functional) cyclic carbonates in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.

[25] Further, the present invention provides a process for cross linking of polycarbonate prepared from mixture of (functional) cyclic carbonates to cross linked polycarbonate through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.

[26] Further, the present invention provides cross linked polycarbonate prepared through polycarbonate prepared from mixture of (functional) cyclic carbonates through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.

Advantageous Effects of Invention

[27] According to the present invention, there are provided novel materials of polycarbonates having unique properties and structures, and the production process thereof which provides a mild environment-friendly process without using phosgene, other chlorinated materials, and bisphenol.

Brief Description of Drawings

[28] Figure 1 shows general polymerization process from six-membered dicyclic carbonates.

- [29] Figure 2 shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of diTMP dicyclic carbonate (diTMPdiCC) at 110°C. (A) diTMPdiCC, (B) product at 30 min of ROP, (C) product at 120 min in ROP.
- [30] Figure 3 shows general polymerization process from allylated cyclic carbonate.
- [31] Figure 4 shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of allylated trimethylolpropane cyclic carbonate (TMPME CC) prepared from trimethylolpropane allylether (TMPME), where (A) is TMPME, (B) is TMPME cyclic carbonate (TMPME CC), (C) is polycarbonate prepared from TMPME CC, (D) is pentaerythritol tetra(3-mercaptopropionate) (PETMP), and (E) is polymer from reaction of (C) with (D) by thermal polymerization.
- [32] Figure 5 shows general polymerization process from allylated cyclic carbonate via prepolymer.
- [33] Figure 6 shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of allylated trimethylolpropane cyclic carbonate (TMPME CC) prepared from trimethylolpropane allylether (TMPME), where (A) is TMPME cyclic carbonate (CC), (B) is prepolymer prepared from reaction of TMPME CC and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) by thermal reaction, (C) is polycarbonate prepared from prepolymer (B) by ROP.
- [34] Figure 7 shows general direct polymerization process from allylated cyclic carbonate.
- [35] Figure 8 shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of allylated trimethylolpropane cyclic carbonate (TMPME CC), where (A) is TMPME cyclic carbonate (CC), (B) is polycarbonate prepared from TMP CC (A) with pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) by thermal reaction and ROP.
- [36] Figure 9 shows general polymerization process from (meth)acrylated cyclic carbonate.
- [37] Figure 10 shows FTIR spectra where (A) is TMPmMA, (B) is TMPmMA cyclic carbonate (CC), (C) is polycarbonate prepared from TMPmMA CC.
- [38] Figure 11 shows FTIR spectra where (A) is mixture of TMPmMA and TMPCC, (B) is polycarbonate prepared from TMPmMACC and TMPCC, (C) is crosslinked polycarbonate in methacrylate group from (C).

Best Mode for Carrying out the Invention

- [39] The present invention relates to a process for ROP of dicyclic carbonate, e.g. diTMP diCC and diTME diCC to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [40] Further, the present invention relates to a polycarbonate prepared from dicyclic

carbonate, e.g. diTMP diCC and diTME diCC by ROP in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.

- [41] Further, the present invention relates to a process for ROP of allylated cyclic carbonate, e.g. TMPME CC and TMEME CC to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [42] Further, the present invention relates to a polycarbonate prepared from allylated cyclic carbonate, e.g. TMPME CC and TMEME CC by ROP in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [43] Further, the present invention relates to a process for cross linking of polycarbonate prepared from allylated cyclic carbonate, e.g. TMPME CC and TMEME CC to cross linked polycarbonate through thermal reaction of polycarbonate with thiol compound in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction with thiol compound in presence of initiator.
- [44] Further, the present invention relates to cross linked polycarbonate prepared through polycarbonate prepared from allylated cyclic carbonate, e.g. TMPME CC and TMEME CC through thermal reaction of polycarbonate with thiol compound in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction of polycarbonate with thiol compound in presence of initiator.
- [45] Further, the present invention relates to a process for thermal reaction of allylated cyclic carbonate, e.g. TMPME CC and TMEME CC with thiol compound to prepolymer in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [46] Further, the present invention relates to prepolymer prepared through thermal reaction of allylated cyclic carbonate, e.g. TMPME CC and TMEME CC with thiol compound in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or with thiol compound by UV reaction in presence of initiator.
- [47] Further, the present invention relates to a process for direct (one-pot) preparation of cross linked polycarbonate from reaction of allylated cyclic carbonate, e.g. TMPME CC and TMEME CC with thiol compound in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [48] Further, the present invention relates to a process for ROP of (meth)acrylated cyclic

carbonate, e.g. TMPmMA CC, TMemMA CC, TMPmA CC and TMemA CC to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.

- [49] Further, the present invention relates to a polycarbonate prepared from (meth)acrylated cyclic carbonate, e.g. TMPmMA CC, TMemMA CC, TMPmA CC and TMemA CC by ROP in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [50] Further, the present invention relates to a process for cross linking of polycarbonate prepared from (meth)acrylated cyclic carbonate, e.g. TMPmMA CC, TMemMA CC, TMPmA CC and TMemA CC to cross linked polycarbonate through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.
- [51] Further, the present invention relates to cross linked polycarbonate prepared through polycarbonate prepared from (meth)acrylated cyclic carbonate, e.g. TMPmMA CC, TMemMA CC, TMPmA CC and TMemA CC through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.
- [52] Further, the present invention relates to a process for ROP of mixture of (functional) cyclic carbonates to polycarbonate in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [53] Further, the present invention relates to polycarbonates prepared from mixture of (functional) cyclic carbonates in presence of catalyst at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C.
- [54] Further, the present invention relates to a process for cross linking of polycarbonate prepared from mixture of (functional) cyclic carbonates to cross linked polycarbonate through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.
- [55] Further, the present invention relates to cross linked polycarbonate prepared through polycarbonate prepared from mixture of (functional) cyclic carbonates through thermal reaction of polycarbonate in presence of initiator at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C, or through UV reaction in presence of initiator.

- [56] A more complete appreciation of the invention, and many of the attendant advantages thereof, will be readily apparent and better understood by reference to the following detailed description and figures. This invention is directed to aliphatic polycarbonates to be used as plastics and resins, and a method of manufacturing polycarbonates without using phosgene and bisphenol (Figure 1, 3 and 5).
- [57] **Ring opening polymerization of cyclic carbonates with catalysts and initiator**
- [58] Cyclic carbonate can be selected from general formula in Figure 1, 3 and 5. DiTMP-diCC and di-trimethylolethane dicyclic carbonate (DiTME-diCC), TMPME CC, trimethylolethane allylether cyclic carbonate (TMEME CC), TMPmMA CC, trimethylolethane methacrylate cyclic carbonate (TMEmMA CC), trimethylolethane acrylate cyclic carbonate TMPmA CC, and trimethylolethane acrylate cyclic carbonate (TMEmA CC) are preferable examples. Cyclic carbonate can be polymerized by ROP using catalysts and initiators at increased temperature. Polycarbonates were formed by the reaction. The process can be carried out in mould to provide the corresponding plastic shapes, and by extruders. Typical organic solvents can be used, but are not necessary for the reaction. The ROP may be performed in solution and any organic solvent selected from the group consisting of C1-C10 alcohols (e.g. methanol and ethanol), C1-C10 hydrocarbone (e.g. n-hexane), ether (e.g. diethylether), acetonitrile, chlorohydrocarbones (dichloromethane, chloroform), dimethylsulfoxide, and a mixture thereof may be used.
- [59] Heterogeneous and homogeneous catalysts are used according to the invention. An inorganic and organometallic catalysis can be selected from various proficient systems based on metal centers, such as sodium, potassium, zinc, magnesium, calcium, or rare-earth metals, bearing suitable ancillary ligands. Also organocatalysts can be used to lead ROP of dicyclic carbonates, and include commercially available amine (4-N,N-dimethylaminopyridine), guanidines (1,5,7-triazabicyclo-[4.4.0]dec-5-ene, phosphazene [2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine), amidine (1,8-Diazabicycloundec-7-ene), tertiary amines (dimethylethanolamine), N-heterocyclic carbenes, and bifunctional thiourea-tertiary amine catalysts. These organocatalysts are used in the presence of an alcohol. An alcohol such as benzyl alcohol, 1,3-propanediol, glycerol that acts both as a co-initiator and a chain-transfer agent, can be used with catalysts. Polycarbonates were formed by the reaction.
- [60] Catalyst can preferably be used at a ratio of 0.001 to 100 wt% of cyclic carbonate. The weight ratio of used catalyst to cyclic carbonate is not limited. But the ratio can preferably be used at a ratio of 0.001 to 100 wt% such as 0.001, 0.01, 0.1, 1, 10 and 100 wt%, or even more preferred 0.01 to 1 wt%. The weight ratio of used alcohols to cyclic carbonate is not limited. But the ratio can preferably be used at a ratio of 0.01 to

- 100 wt% such as 0.01, 0.1, 1, 10 and 100 wt%, or even more preferred 0.1 to 1 wt%.
- [61] Such ROP could be carried out at ambient temperature (room temperature, RT), or at temperature ranging from ambient to 300°C, preferably 80 to 150°C. As a non-limited example the reaction time could be 1 minute or longer, or 1 hour or longer, or 1 day or longer, 10 days or longer.
- [62] General additives such as hardener, softener, catalyst, pigment and binder can be used in the plastics, sheets, chips and resins formation.
- [63] **Cross linking polymerization in** allyl and (meth)acryl group of cyclic carbonates with catalyst
- [64] The obtained ring opened polycarbonate of e.g. TMPME CC and TMEME CC may be further polymerized via an ene functional group in allyl group (General scheme in Figure 3). The ring opened polycarbonate of e.g. TMPME and TMEME may be reacted with thiol compounds using UV or thermal energy. The thiol compounds may be chosen from dithiols, such as 1,2-ethylenedithiol; or trithiols, such as trimethylpropane tris(3-mercaptopropionate); tetrathiol, such as pentaerythritol tetrakis(3-mercaptopropionate); and polythiols. The UV or thermal reaction may be initiated by an initiator.
- [65] The obtained ring opened polycarbonate of e.g. TMPmMA CC, TMEmMA CC, TMPmA CC and TMEmA may be polymerized via an (meth)acrylate functional group (General scheme in Figure 5). The ring opened polycarbonate of e.g. TMPmMA CC, TMEmMA CC, TMPmA CC and TMEmA may be polymerized by UV or thermal reaction. Any typical polymerization method may be used in the polymerization of methacrylate group by UV and/or thermal reaction in the absence or presence of an initiator and/or catalyst. The UV or thermal reaction may be initiated by an initiator.
- [66] An initiator may be used in the reaction and polymerization process in above cross linking polymerizations in allyl and (meth)acryl group, and may be selected from the group azo compounds of azobisisobutyronitrile (AIBN) and 1,1'-azobis(cyclohexanecarbonitrile) (ABCN), 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure®), and organic peroxides of di-ter-butyl peroxide and benzoyl peroxide.
- [67] The reaction and application may be performed in solution form and any organic solvent may be used. However, preferred solvents are alcohols (e.g. methanol, ethanol and propanol), (cyclic) ethers (e.g. diethyl ether and THF), ketones (e.g. acetone, ethylmethylketone), toluene, acetonitrile, halogenated alkane (dichloromethane and chloroform), dimethylformamide, and pyridine or mixtures of the same or mixtures containing said solvents. Use of solvent provides the homogenization, polymerization and coating application.
- [68] If the reaction and polymerization is performed using thermal energy the temperature

may be at least 20°C, such as at least 90°C, at least 100°C, at least 120°C, at least 140°C, or at least 160°C.

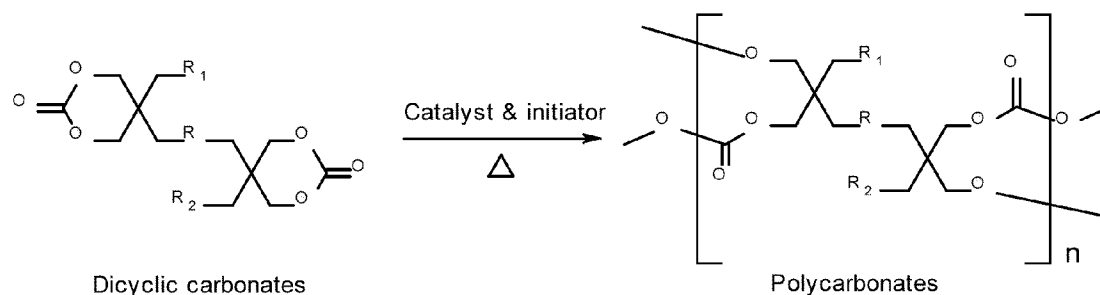
[69] **Determination of physical properties for resulting polycarbonates**

[70] For materials in accordance with the present invention, the thermal property (glass transition temperature, T_g) was measured by differential scanning calorimeter (DSC). The apparent transparency of the material was determined, and the results were indicated with leads ranging in transparency from 1 (low) to 5 (high transparency, colorless). The formation of linear carbonate group from cyclic carbonate was determined from samples collected from polymerized material by FT-IR analysis.

Mode for the Invention

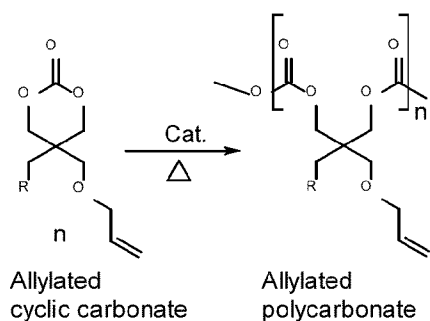
[71] In one embodiment, the present invention relates to a process for preparing polycarbonate comprising polymerizing dicyclic carbonate, allylated cyclic carbonate, (meth)acrylated cyclic carbonate, or a mixture thereof as shown below to polycarbonate as shown below through Ring Open Polymerization (ROP) in presence of catalyst at temperature ranging from ambient temperature (room temperature, RT) to 300°C. according to the schemes (I) - (III) given below:

[72]



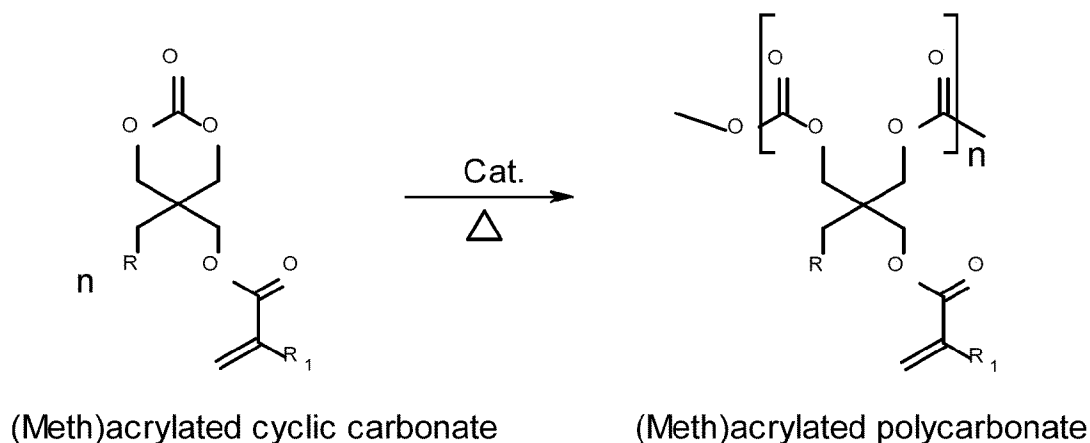
[73] Scheme (I)

[74]



[75] Scheme (II)

[76]



[77] Scheme (III)

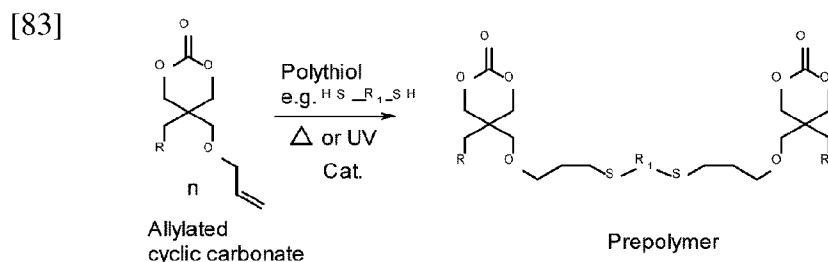
[78] wherein in the scheme (I), R = oxygen (ether), C1-10 alkyl, C3-10 ketone, C3-10 ester. R₁, R₂ = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively, and n=10-10000; in the scheme (II), R = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy or C2-10 carboxyl group, respectively, m=10-10000, and n=10-10000; in the scheme (III), R and R₁ = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively, m=10-10000, and n=10-10000.

[79] In preferred embodiments, the above process for preparing polycarbonate can comprises thermally reacting polycarbonate prepared from allylated cyclic carbonate, (meth)acrylated cyclic carbonate, or a mixture thereof with thiol compound in presence of initiator at temperature ranging from ambient temperature (room temperature, RT) to 300°C, or UV reacting polycarbonate with thiol compound in presence of initiator, thus obtaining cross linked polycarbonate or highly cross linked polycarbonate.

[80] In preferred embodiments, the dicyclic carbonate is di-trimethylolpropane dicyclic carbonate (diTMP diCC), di-trimethylolethane dicyclic carbonate (diTME diCC) or a mixture thereof, the allylated cyclic carbonate is trimethylolpropane allylether cyclic carbonate (TMPME CC), trimethylolethane allylether cyclic carbonate (TMEME CC) or a mixture thereof, and the (meth)acrylated cyclic carbonate is (meth)acrylated trimethylolpropane cyclic carbonate (TMPmMA CC), trimethylolethane methacrylate cyclic carbonate (TMEmMA CC), trimethylolethane acrylate cyclic carbonate (TMPmA CC), trimethylolethane acrylate cyclic carbonate (TMEmA CC) or a mixture thereof.

[81] In another embodiment, the present invention relates to a polycarbonate prepared by the process for preparing polycarbonate according to the present invention.

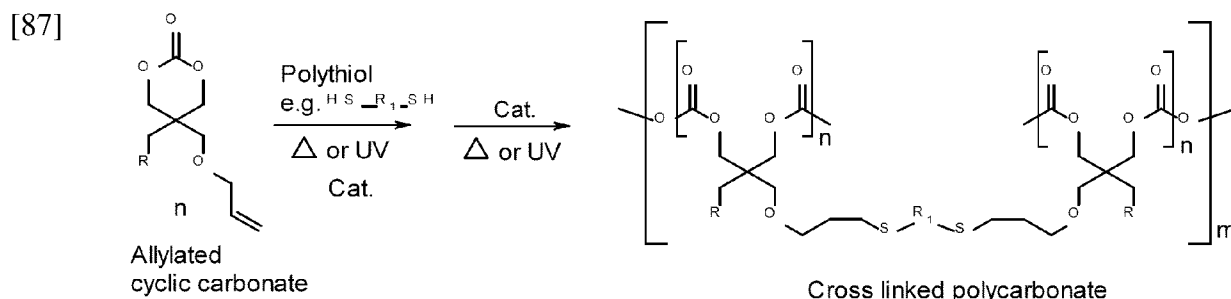
[82] In further embodiment, the present invention relates to a process for preparing prepolymer comprising reacting allylated cyclic carbonate as shown below with thiol compound through thermal reaction in presence of catalyst at temperature ranging from ambient temperature (room temperature, RT) to 300°C, or through UV reaction in presence of initiator according to the scheme given below:



[84] wherein R = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively; Polythiol = alkylthiol (R_1 = C1-20 alkyl), trimethylolpropane tri(3-mercaptopropionate), glycol di(3-mercaptopropionate), glyceryl dithioglycolate, glycol dimercaptoacetate, trimethylolpropane trimercaptoacetate, pentaerythritol tetramercaptoacetate, pentaerythritol tetra(3-mercaptopropionate), or their derivatives.

[85] In further embodiment, the present invention relates to a prepolymer prepared by the a process for preparing prepolymer according to the present invention.

[86] In further embodiment, the present invention relates to a process for directly (one-pot) preparing cross linked polycarbonate comprising reacting allylated cyclic carbonate as shown below with thiol compound through thermal reaction in presence of catalyst at temperature ranging from ambient temperature (room temperature, RT) to 300°C or through UV reaction in presence of initiator according to the scheme given below:



[88]

[89] wherein R = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively; Polythiol = alkylthiol (R_1 = C1-20 alkyl), trimethylolpropane tri(3-mercaptopropionate), glycol di(3-mercaptopropionate), glyceryl

dithioglycolate, glycol dimercaptoacetate, trimethylolpropane trimercaptoacetate, pentaerythritol tetramercaptoacetate, pentaerythritol tetra(3-mercaptopropionate), or their derivatives; $m=10-10000$; and $n=10-10000$.

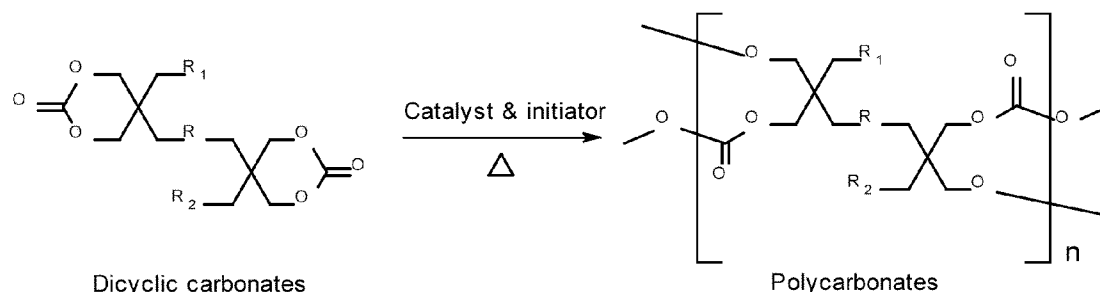
[90] In further embodiment, the present invention relates to a cross linked polycarbonate prepared by the process for preparing cross linked polycarbonate according to the present invention.

[91] In the preferred embodiments, the thiol compound used in the process for preparing cross linked polycarbonate is chosen from dithiols, trithiols, tetrathiols, and polythiols. Preferably, the above thiol compound is chosen from 1,2-ethylenedithiol, trimethylolpropane tris(3-mercaptopropionate), and pentaerythritol tetrakis(3-mercaptopropionate).

[92] 1. Polymerization of dicyclic carbonates

[93] In the present invention, cyclic carbonates are dicyclic carbonates having six-membered rings from polyols such as di-trimethylolpropane (diTMP), di-trimethylolethane (diTME) and derivatives thereof. Polycarbonates according to the present invention can be prepared by polymerizing dicyclic carbonates as shown in the scheme below (see also Figure 1):

[94]



[95] wherein R = oxygen (ether), C1-10 alkyl, C3-10 ketone, C3-10 ester. $R_1, R_2 = H$, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively, and $n=10-10000$.

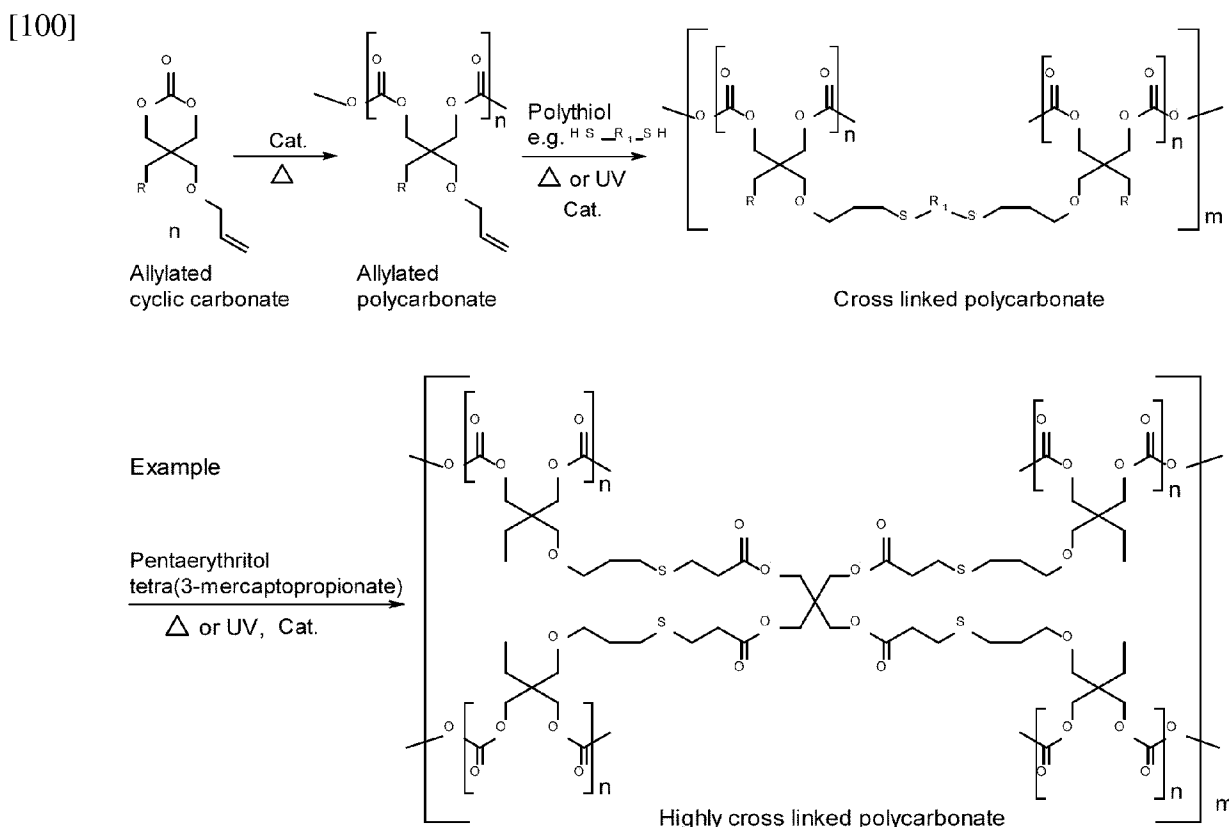
[96] Referring to figure 2, figure 2 shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of diTMP dicyclic carbonate (diTMPdiCC) at 110°C. (A) diTMPdiCC, (B) product at 30 min of ROP, (C) product at 120 min in ROP. P1 indicates C=O stretching band peak at 1765-1720 cm^{-1} . P2 indicates linear C-O-C asymmetric stretching band peak at 1290-1180 cm^{-1} . FT-IR analyses were performed using Nicolet-iS5 (Thermo Scientific, USA).

[97] As a representative polymerization, the ROP of diTMP diCC was performed with 0.1% (w/w) 4-(dimethylamino)pyridine (DMAP) as a catalyst and 1% (w/w) 1,3-propanediol as an initiator/chain transfer agent at 110°C in a thermoshaker. In

Figure 2, FT-IR spectra show the peak shifts of functional groups in the reaction at 110°C. P1 indicates peak shift of 9 cm⁻¹ from cyclic carbonyl group of diTMP diCC at 1731 cm⁻¹ to linear carbonyl group of polycarbonate at 1740 cm⁻¹. C-O-C asymmetric stretching band peak is typically appeared at 1290-1180cm⁻¹. The functionality change (P2) of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1229 cm⁻¹ with decreasing intensity in range of 1100-1200 cm⁻¹. The hydroxyl group at 3400 cm⁻¹ did not appear and indicated that the polymerization and crosslinking was quickly achieved after opening of the cyclic carbonate ring.

[98] 2. Polymerization of allylated cyclic carbonates

[99] In the present invention, cyclic carbonates are functionalized cyclic carbonates having an allyl group in polyols such as trimethylolpropane (TMP), trimethylolethane (TME) and derivatives thereof. Polycarbonates according to the present invention can be prepared by polymerizing functionalized cyclic carbonates having an allyl group as shown in the scheme below (see also Figure 3):



[101] wherein R = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy or C2-10 carboxyl group, respectively; Polythiol = alkylthiol (R₁ = C1-20 alkyl), trimethylolpropane tri(3-mercaptopropionate), glycol di(3-mercaptopropionate), Glyceryl dithioglycolate, glycol dimercaptoacetate, trimethylolpropane trimercaptoacetate, pentaerythritol tetramercaptoacetate, pentaerythritol tetra(3-mercaptopropionate), or their

derivatives; $m=10-10000$; and $n=10-10000$. Example shows highly cross linked polycarbonate prepared from reaction of allylated polycarbonate and pentaerythritol tetra(3-mercaptopropionate).

[102] Referring to figure 4, figure 4 shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of allylated trimethylolpropane cyclic carbonate (TMPME CC) prepared from trimethylolpropane allylether (TMPME), where (A) is TMPME, (B) is TMPME cyclic carbonate (TMPME CC), (C) is polycarbonate prepared from TMPME CC, (D) is pentaerythritol tetra(3-mercaptopropionate) (PETMP), and (E) is polymer from reaction of (C) with (D) by thermal polymerization. FT-IR spectra show the peak shifts of functional groups in each reaction step. (A) TMPME: the strong broad peak in 3364 cm^{-1} indicates -OH group. (B) TMPME CC: a new peak at 1747 cm^{-1} indicates carbonyl group of cyclic carbonate, and the strong broad peak of -OH group in 3364 cm^{-1} disappeared with formation of cyclic carbonate. (C) Polycarbonate from TMPME CC: a peak at 1237 cm^{-1} is strongly increased, which is C-O-C asymmetric stretching. (D) Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) used as a cross-linker. (E) Highly cross linked polycarbonate from reaction of (C) with (D): A peak at 900 cm^{-1} in (A, B and C), which is C-H of mono-substituted alkene, disappeared by reaction of alkene with thiol group of PETMP. A peak at 1744 cm^{-1} in (B,C) is shifted to 1735 cm^{-1} (E). FT-IR analyses were performed using Nicolet-iS5 (Thermo Scientific, USA).

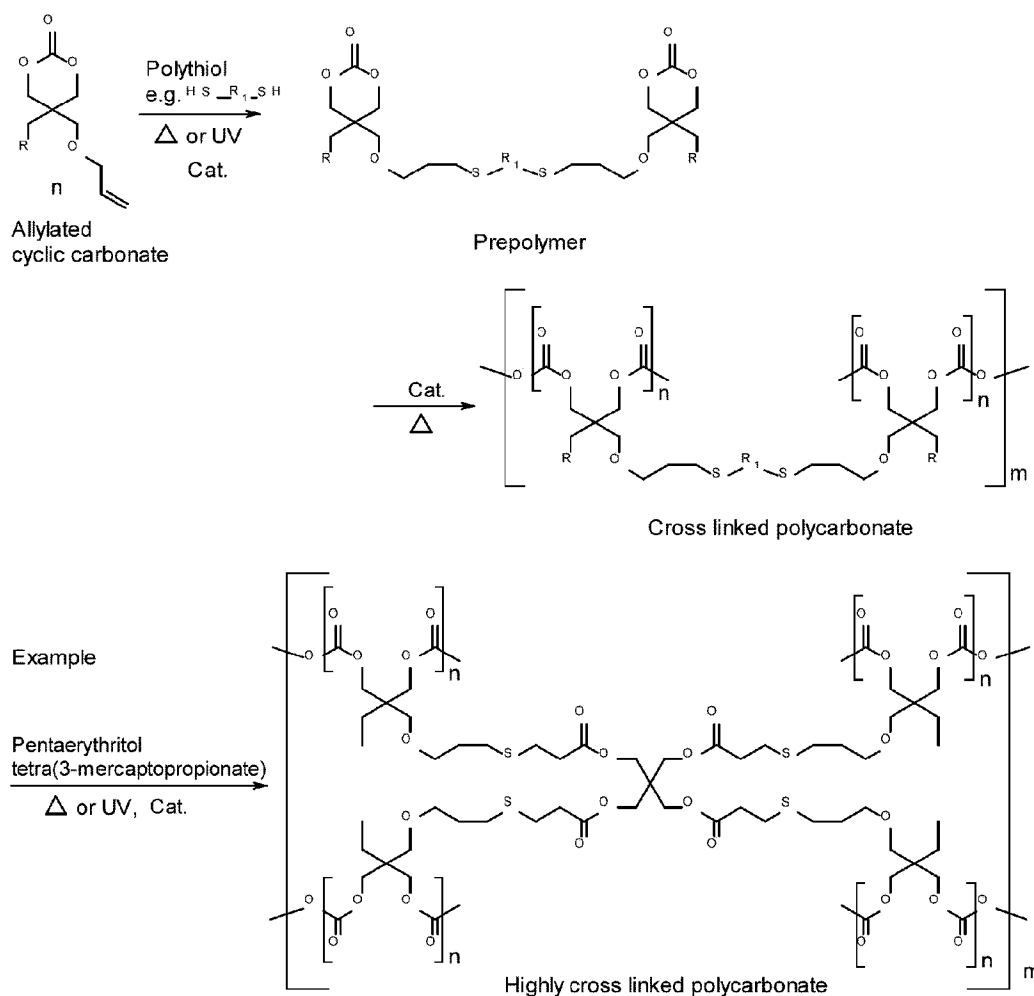
[103] As a representative polymerization, the ROP of TMPME CC (200mg) was performed with 4-(dimethylamino)pyridine (DMAP, 1mg) as a catalyst and 1,3-propanediol (0.01mL) as an initiator/chain transfer agent at 90°C in a thermoshaker. In Figure 4, FT-IR spectra show the peak shifts of functional groups in the reaction at 110°C . C-O-C asymmetric stretching band peak is typically appeared at $1290-1180\text{ cm}^{-1}$ (P3). The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1237 cm^{-1} with decreasing intensity in range of $1100-1200\text{ cm}^{-1}$. The hydroxyl group at 3400 cm^{-1} did not appear and indicated that the polymerization and crosslinking was quickly achieved after opening of the cyclic carbonate ring. Resulting polycarbonate (C) was reacted with a cross linker, PETMP (122mg, equivalent to TMPMECC) with azobisisobutyronitrile (AIBN, 3mg in 0.03mL acetonitrile) as a initiator at 90°C to highly cross linked polycarbonate (E). In P4, a peak at 900 cm^{-1} in (A,B and C), which is C-H of mono-substituted alkene, disappeared by reaction of alkene with thiol group of PETMP.

[104] 3. Polymerization of allylated cyclic carbonates via prepolymer

[105] In the present invention, cyclic carbonates are functionalized cyclic carbonates having an allyl group in polyols such as trimethylolpropane (TMP), trimethylolethane (TME) and derivatives thereof. Polycarbonates according to the present invention can

be prepared by polymerizing functionalized cyclic carbonates having an allyl group via prepolymer as shown in the scheme below (see also Figure 5):

[106]



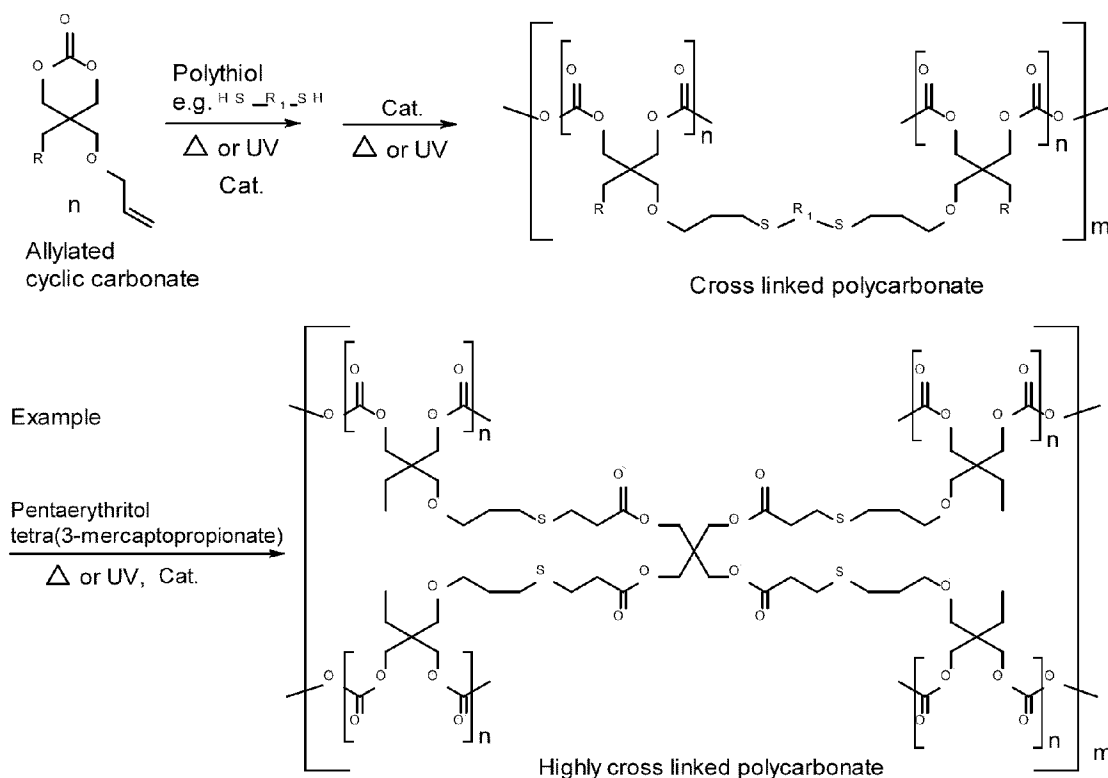
[107] wherein R = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively; Polythiol = alkylthiol (R₁ = C1-20 alkyl), trimethylolpropane tri(3-mercaptopropionate), glycol di(3-mercaptopropionate), glyceryl dithioglycolate, glycol dimercaptoacetate, trimethylolpropane trimercaptoacetate, pentaerythritol tetramercaptoacetate, pentaerythritol tetra(3-mercaptopropionate), or their derivatives; m=10-10000; and n=10-10000. Example shows highly cross linked polycarbonate prepared from reaction of allylated polycarbonate and pentaerythritol tetra(3-mercaptopropionate).

[108] Referring to figure 6, figure 6 shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of allylated trimethylolpropane cyclic carbonate (TMPME CC) prepared from trimethylolpropane allylether (TMPME), where (A) is TMPME cyclic carbonate (CC), (B) is prepolymer prepared from reaction of TMPME CC and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) by

thermal reaction, (C) is polycarbonate prepared from prepolymer (B) by ROP.

- [109] FT-IR spectra show the peak shifts of functional groups in each reaction step. (A) TMPME CC: A peak at 1737 cm^{-1} indicates carbonyl group of cyclic carbonate, and a peak at 927 cm^{-1} indicates C-H of mono-substituted alkene. (B) Prepolymer (TMPMECC-PETMP): The alkene peak at 927 cm^{-1} disappeared by reaction of alkene with thiol group of PETMP. (C) Polycarbonate from prepolymer (B): A peak at 1240 cm^{-1} is strongly increased, which is C-O-C asymmetric stretching by ROP of cyclic carbonate. FT-IR analyses were performed using Nicolet-iS5 (Thermo Scientific, USA).
- [110] As a representative polymerization, the thermal reaction of TMPME CC (200mg) with a cross linker, PETMP (122mg, equivalent to TMPMECC) with azobisisobutyronitrile (AIBN, 3mg in 0.03mL acetonitrile) as a initiator at 90°C to prepolymer (B). In Figure 6, FT-IR spectra show the peak shifts of functional groups in the reaction at 90°C . In P4 (B), a peak at 927 cm^{-1} in (A), which is C-H of mono-substituted alkene, disappeared by reaction of alkene with thiol group of PETMP.
- [111] The ROP of prepolymer (B) was performed with 4-(dimethylamino)pyridine (DMAP, 3mg) as a catalyst and 1,3-propanediol (0.03mL) as an initiator/chain transfer agent to polycarbonate (C) at 110°C in a thermoshaker. In FT-IR, C-O-C asymmetric stretching band peak is typically appeared at $1290\text{-}1180\text{ cm}^{-1}$ (P3). The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1240 cm^{-1} with decreasing intensity in range of $1100\text{-}1200\text{ cm}^{-1}$.
- [112] 4. Direct polymerization of allylated cyclic carbonates
- [113] In the present invention, cyclic carbonates are functionalized cyclic carbonates having an allyl group in polyols such as trimethylolpropane (TMP), trimethylolethane (TME) and derivatives thereof. Polycarbonates according to the present invention can be prepared by polymering functionalized cyclic carbonates having an allyl group as shown in the scheme below (see also Figure 7):

[114]



[115] wherein R = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively; Polythiol = alkylthiol (R_1 = C1-20 alkyl), trimethylolpropane tri(3-mercaptopropionate), glycol di(3-mercaptopropionate), glyceryl dithioglycolate, glycol dimercaptoacetate, trimethylolpropane trimercaptoacetate, pentaerythritol tetramercaptoacetate, pentaerythritol tetra(3-mercaptopropionate), or their derivatives; $m=10-10000$; and $n=10-10000$. Example shows highly cross linked polycarbonate prepared from reaction of allylated polycarbonate and pentaerythritol tetra(3-mercaptopropionate).

[116] Referring to figure 8, it shows FT-IR spectra of the reaction components and polycarbonate products formed during ROP of allylated trimethylolpropane cyclic carbonate (TMPME CC), where (A) is TMPME cyclic carbonate (CC), (B) is polycarbonate prepared from TMP CC (A) with pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) by thermal reaction and ROP.

[117] FT-IR spectra show the peak shifts of functional groups in each reaction step. (A) TMPME CC: A peak at 1737 cm^{-1} indicates carbonyl group of cyclic carbonate, and a peak at 927 cm^{-1} indicates C-H of mono-substituted alkene. (B) Polycarbonate: The alkene peak at 927 cm^{-1} disappeared by reaction of alkene with thiol group of PETMP. A peak at 1240 cm^{-1} is strongly increased, which is C-O-C asymmetric stretching by ROP of cyclic carbonate. FT-IR analyses were performed using Nicolet-iS5 (Thermo Scientific, USA).

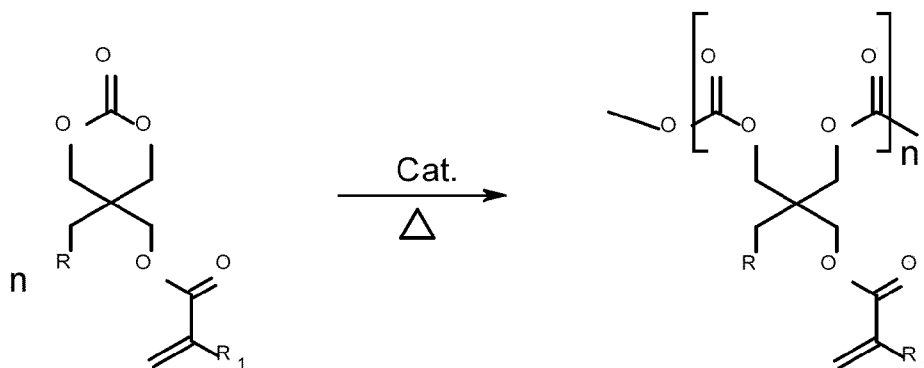
[118] As a representative polymerization, the polymerization of TMPME CC (200mg) with a cross linker, PETMP (122mg, equivalent to TMPMECC) was performed with azobisisobutyronitrile (AIBN, 3mg in 0.03mL acetonitrile) as a initiator and 4-(dimethylamino)pyridine (DMAP, 3mg) as a catalyst and 1,3-propanediol (0.03mL) as an initiator/chain transfer agent at 110°C in a thermoshaker.

[119] In Figure 8, FT-IR spectra show the peak shifts of functional groups in the reaction at 110°C. In P4 (B), a peak at 927 cm⁻¹ in (A), which is C-H of mono-substituted alkene, disappeared by reaction of alkene with thiol group of PETMP. C-O-C asymmetric stretching band peak is typically appeared at 1290-1180cm⁻¹(P3). The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1240 cm⁻¹ with decreasing intensity in range of 1100-1200 cm⁻¹.

[120] 5. Polymerization of (meth)acrylated cyclic carbonates

[121] In the present invention, cyclic carbonates are functionalized cyclic carbonates having an (meth)acrylic group in polyols such as trimethylolpropane (TMP), trimethylolethane (TME) and derivatives thereof. Polycarbonates according to the present invention can be prepared by polymerizing functionalized cyclic carbonates having an (meth)acrylic group as shown in the scheme below (see also Figure 9):

[122]



(Meth)acrylated cyclic carbonate

(Meth)acrylated polycarbonate

[123] wherein R and R₁ = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively.

[124] Referring to figure 10, it shows FTIR spectra where (A) is TMPmMA, (B) is TMPmMA cyclic carbonate (CC), (C) is polycarbonate prepared from TMPmMA CC. FT-IR spectra show the peak shifts of functional groups in each reaction step.

[125] FT-IR spectra of the reaction components and polycarbonate products formed during ROP of (meth)acrylated trimethylolpropane cyclic carbonate (TMPmMA CC) prepared from trimethylolpropane methacrylate (TMPmMA), where (A) is TMPmMA, (B) is TMPmMA cyclic carbonate (TMPMA CC), (C) is polycarbonate prepared from TMPmMA CC by thermal polymerization. FT-IR spectra show the peak shifts of

functional groups in each reaction step. (A) TMPmMA: the strong broad peak at 3364 cm^{-1} indicates -OH group, and doublet peak in 1699 cm^{-1} indicates carbonyl group of carbonate and methacrylate. (B) TMPmMA CC: a new peak at 1747 cm^{-1} indicates carbonyl group of cyclic carbonate, and the strong broad peak of -OH group at 3364 cm^{-1} disappeared with formation of cyclic carbonate. (C) Polycarbonate from TMPmMA CC: a peak at 1239 cm^{-1} is strongly increased, which is C-O-C asymmetric stretching, and a peak of carbonyl group of cyclic carbonate at 1747 cm^{-1} is shifted to linear carbonyl group at 1723 cm^{-1} . FT-IR analyses were performed using Nicolet-iS5 (Thermo Scientific, USA).

- [126] As a representative polymerization, the ROP of TMPmMA CC (200mg) was performed with 4-(dimethylamino)pyridine (DMAP, 1mg) as a catalyst and 1,3-propanediol (0.01mL) as an initiator/chain transfer agent at 90°C in a thermoshaker. In Figure 10, FT-IR spectra show the peak shifts of functional groups in the reaction at 90°C . C-O-C asymmetric stretching band peak typically appeared at $1290\text{--}1180\text{ cm}^{-1}$ (P3). The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1239 cm^{-1} with decreasing intensity in range of $1100\text{--}1200\text{ cm}^{-1}$. The hydroxyl group at 3364 cm^{-1} did not appear and indicated that the polymerization was quickly achieved after opening of the cyclic carbonate ring. Peaks of carbonyl group are shifted after polymerization.

[127] 6. Polymerization of mixtures of (functional) cyclic carbonates

- [128] Functional cyclic carbonates can be mixed at different ratio and polymerized with other functional cyclic carbonates or cyclic carbonates to obtain different physical properties in ring-opening polymerization. (Functional) cyclic carbonate can be selected from diTMPdiCC, TMPmMA CC, TMPMECC, trimethylolpropane cyclic carbonate (TMPCC), trimethylene carbonate, 1-methyl-trimethylene carbonate, 2-methyl-trimethylene carbonate, 2-(methoxycarbonyl)-2-methyl-trimethylene carbonate, 1,1-dimethyl-trimethylene carbonate, but not limited. For instance, but not limited, diTMPdiCC and TMPmMA CC, diTMPdiCC and 1-methyl-trimethylene carbonate, TMPMECC and 1,1-dimethyl-trimethylene carbonate, and TMPMA CC and TMPCC.

- [129] Referring to figure 11, it shows FTIR spectra where (A) is mixture of TMPmMA and TMPCC, (B) is polycarbonate prepared from TMPmMA CC and TMPCC, (C) is crosslinked polycarbonate in methacrylate group from (C). FT-IR spectra show the peak shifts of functional groups in each reaction step.

- [130] As a representative polymerization, the ROP of mixture of TMPmMA CC (91mg) and trimethylolpropane cyclic carbonate (65mg) was performed with triethylamine (3mg) as a catalyst and 1,3-propanediol (0.003mL) as an initiator/chain transfer agent at 90°C in a thermoshaker. Resulting polycarbonate was further polymerized and so-

lidified using UV initiator by UV for 1 min.

- [131] In Figure 11, FT-IR spectra show the peak shifts of functional groups in the reaction at 90°C. C-O-C asymmetric stretching band peak typically appeared at 1290-1180cm⁻¹. The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1239 cm⁻¹ with decreasing intensity in range of 1100-1200 cm⁻¹. The hydroxyl group at 3364 cm⁻¹ did not appear and indicated that the polymerization was quickly achieved after opening of the cyclic carbonate ring. Peaks of carbonyl group are shifted after polymerization.

[132] **Examples**

- [133] The present invention is further explained in more detail with reference to the following examples. These examples, however, should not be interpreted as limiting the scope of the present invention in any manner.

[134] **Example 1.** Polycarbonate synthesis from diTMPdiCC with FT-IR monitoring

- [135] 200 mg diTMPdiCC was placed in 4mL glass vial and heated at 110°C using thermomixer. After melting, 4 mg 1,3-propanediol and 0.5 mg DMAP were added. The ROP was monitored using FT-IR at 10, 20, 30, 60 and 120 minutes (Figure 2). The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1229 cm⁻¹ for C-O-C asymmetric stretching band peak with decreasing intensity in range of 1100-1200 cm⁻¹.

[136] **Example 2.** Hardness and Tg of polycarbonate from diTMPdiCC

- [137] 500 mg diTMPdiCC was placed in 20mL glass vial and heated at 120°C in oven. After melting, 10 mg 1,3-propanediol and 5 mg DMAP were added. After 2 hr reaction, solid material was cooled and stored in room temperature. Hardness was 3.9 kg (force) in 15% strain and compression mode, and Tg was 86.7°C by DSC analysis.

[138] **Example 3.** Polycarbonate from diTMPdiCC in mould

- [139] 3000 mg diTMPdiCC was placed in aluminium mould and heated at 120°C in an oven. After melting, 20 mg 1,3-propanediol and 5 mg DMAP were added. After 2 hr reaction, the solid material was cooled and stored in room temperature. A piece of polycarbonate was obtained with high transparency (higher than 4).

[140] **Example 4.** Polycarbonate from TMPME CC with FT-IR monitoring

- [141] 200mg TMPME CC was placed in 4mL glass vial and heated at 90°C using thermomixer. 10 mg 1,3-propanediol and 1 mg DMAP were added at 90°C. After 30 minutes, the ROP was monitored using FT-IR. The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1237 cm⁻¹ for C-O-C asymmetric stretching band peak with decreasing intensity in range of 1100-1200 cm⁻¹. The resulting polycarbonate was liquid phase (amorphous) at room temperature.

- [142] **Example 5.** Cross linking polymerization of polycarbonate from TMPME CC with

FT-IR monitoring

- [143] Liquid phase of sample resulting from Example 4 was reacted with a cross linker, PETMP (122mg, equivalent to TMPMECC) using azobisisobutyronitrile (AIBN, 3mg in 0.03mL acetonitrile) at 90°C. After 10 minutes, cross linked polycarbonate (solid phase) was obtained, and the reaction was monitored using FT-IR. By the functionality change, a peak at 900 cm⁻¹, which is C-H of mono-substituted alkene, disappeared by reaction of alkene with thiol group of PETMP.
- [144] **Example 6.** Prepolymer from reaction of TMPME CC with PETMP with FT-IR monitoring
- [145] 200mg TMPME CC with a cross linker, PETMP (122mg, equivalent to TMPMECC) was placed in 4mL glass vial and reacted using azobisisobutyronitrile (AIBN, 3mg in 0.03mL acetonitrile) at 90°C. After 10 minutes, the reaction was monitored using FT-IR. A peak at 927 cm⁻¹, which is C-H of mono-substituted alkene, disappeared by reaction of alkene with thiol group of PETMP. The resulting prepolymer was liquid phase (amorphous) at room temperature.
- [146] **Example 7.** ROP of prepolymer prepared from reaction of TMPME CC with PETMP with FT-IR monitoring
- [147] Liquid phase of sample resulting from Example 6 was polymerized using 30 mg 1,3-propanediol and 3 mg DMAP at 110°C by ROP. After 60 minutes, cross linked polycarbonate (solid phase) was obtained, and the reaction was monitored using FT-IR. The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1240 cm⁻¹ for C-O-C asymmetric stretching band peak with decreasing intensity in range of 1100-1200 cm⁻¹.
- [148] **Example 8.** Direct polymerization of TMPME CC with PETMP with FT-IR monitoring
- [149] 200mg TMPME CC with a cross linker, PETMP (122mg, equivalent to TMPMECC) was placed in 4mL glass vial, and reacted using azobisisobutyronitrile (AIBN, 3mg in 0.03mL acetonitrile), 30 mg 1,3-propanediol and 3 mg DMAP at 110°C. After 60 minutes, cross linked polycarbonate (solid phase) was obtained, the reaction was monitored using FT-IR. A peak at 927 cm⁻¹, which is C-H of mono-substituted alkene, disappeared by reaction of alkene with thiol group of PETMP. The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1240 cm⁻¹ for C-O-C asymmetric stretching band peak with decreasing intensity in range of 1100-1200 cm⁻¹.
- [150] **Example 9.** Polycarbonate from TMPmMA CC with FT-IR monitoring
- [151] 200mg TMPmMA CC was placed in 4mL glass vial and heated at 90°C using thermomixer. 10 mg 1,3-propanediol and 1 mg DMAP were added at 90°C. After 30 minutes, the ROP was monitored using FT-IR. A piece of polycarbonate (solid phase)

was obtained. The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1239 cm^{-1} for C-O-C asymmetric stretching band peak with decreasing intensity in range of 1100-1200 cm^{-1} . The hydroxyl group at 3364 cm^{-1} did not appear and indicated that the polymerization was quickly achieved after opening of the cyclic carbonate ring. Peaks of carbonyl group are shifted after polymerization. Resulting polycarbonate was further polymerized in the methacrylate group on the surface of glass using UV initiator, 1mg 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure®) by UV lamp (365nm).

[152] **Example 10.** Polycarbonate from mixture of (functional) cyclic carbonates with FT-IR monitoring

[153] 91mg TMPmMACC and 65mg TMPCC were placed in 4mL glass vial and heated at 90°C using thermomixer. 0.003mL 1,3-propanediol and 3 mg triethylamine were added at 90°C. After 30 minutes, the ROP was monitored using FT-IR. A Polycarbonate (liquid phase) was obtained. The functionality change of C-O-C group from cyclic carbonate to linear polycarbonate provided a strong new peak at 1230-1240 cm^{-1} for C-O-C asymmetric stretching band peak with decreasing intensity in range of 1100-1200 cm^{-1} . The hydroxyl group at 3364 cm^{-1} did not appear and indicated that the polymerization was quickly achieved after opening of the cyclic carbonate ring. Peaks of carbonyl group are shifted after polymerization.

[154] **Example 11.** Cross-linked polycarbonate from polycarbonate

[155] Resulting polycarbonate from Example 9 was further polymerized and solidified on the surface of glass using UV initiator, 1mg 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure®) by UV lamp (365nm).

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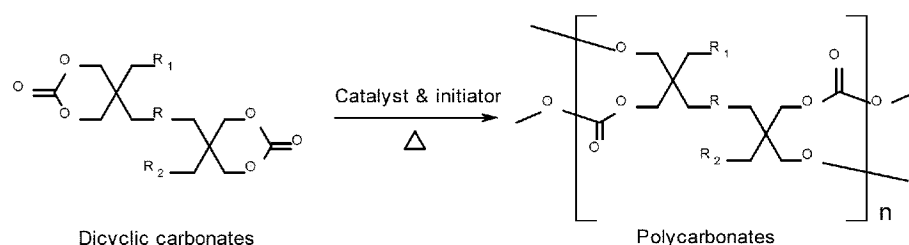
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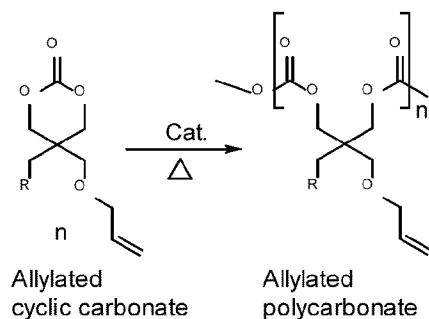
Claims

[Claim 1]

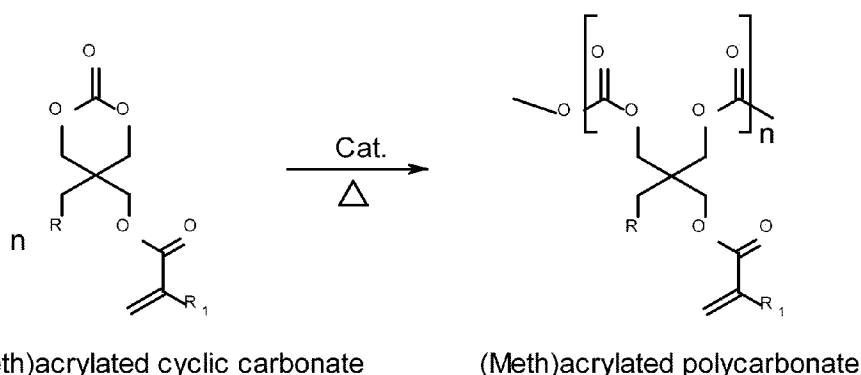
A process for preparing polycarbonate comprising polymerizing dicyclic carbonate, allylated cyclic carbonate, (meth)acrylated cyclic carbonate, or a mixture thereof as shown below to polycarbonate as shown below through Ring Open Polymerization (ROP) in presence of catalyst at temperature ranging from ambient temperature (room temperature, RT) to 300°C. according to the schemes (I) - (III) given below:



Scheme (I)



Scheme (II)



Scheme (III)

wherein in the scheme (I), R = oxygen (ether), C1-10 alkyl, C3-10 ketone, C3-10 ester, R₁, R₂ = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy-carbonyl, C4-10 alkoxy-carbonyloxy and C2-10 carboxyl group, re-

spectively, and $n=10-10000$; in the scheme (II), $R = H$, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy or C2-10 carboxyl group, respectively, $m=10-10000$, and $n=10-10000$; in the scheme (III), R and $R_1 = H$, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively, $m=10-10000$, and $n=10-10000$.

[Claim 2]

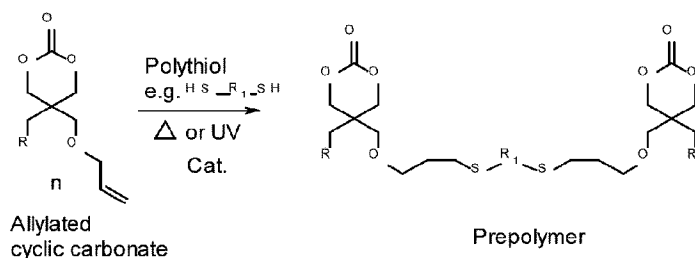
The process as claimed in claim 1, wherein said dicyclic carbonate is di-trimethylolpropane dicyclic carbonate (diTMP diCC), di-trimethylolethane dicyclic carbonate (diTME diCC) or a mixture thereof, said allylated cyclic carbonate is trimethylolpropane allylether cyclic carbonate (TMPME CC), trimethylolethane allylether cyclic carbonate (TME ME CC) or a mixture thereof, and said (meth)acrylated cyclic carbonate is (meth)acrylated trimethylolpropane cyclic carbonate (TMPmMA CC), trimethylolethane methacrylate cyclic carbonate (TME mMA CC), trimethylolethane acrylate cyclic carbonate (TMPm A CC), trimethylolethane acrylate cyclic carbonate (TME m A CC) or a mixture thereof.

[Claim 3]

A polycarbonate prepared by the process according to claim 1 or 2.

[Claim 4]

A process for preparing prepolymer comprising reacting allylated cyclic carbonate as shown below with thiol compound through thermal reaction in presence of catalyst at temperature ranging from ambient temperature (room temperature, RT) to 300°C, or through UV reaction in presence of initiator according to the scheme given below:



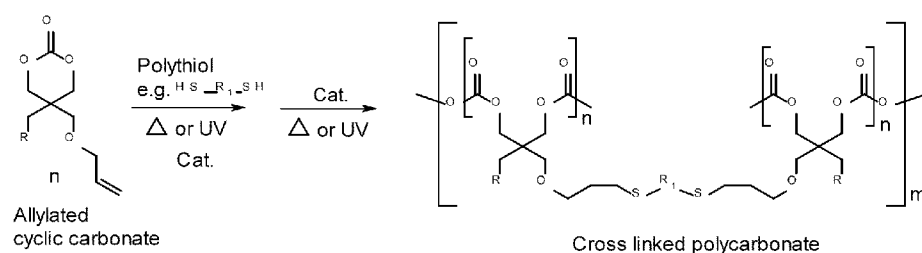
wherein $R = H$, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively; Polythiol = alkylthiol ($R_1 = \text{C1-20 alkyl}$), trimethylolpropane tri(3-mercaptopropionate), glycol di(3-mercaptopropionate), glyceryl dithioglycolate, glycol dimercaptoacetate, trimethylolpropane trimer-captoacetate, pentaerythritol tetramercaptoacetate, pentaerythritol

tetra(3-mercaptopropionate), or their derivatives.

[Claim 5] The process as claimed in claim 4, wherein said allylated cyclic carbonate is TMPME CC, TMEME CC or a mixture thereof.

[Claim 6] A prepolymer prepared by the process according to claim 4 or 5.

[Claim 7] A process for directly (one-pot) preparing cross linked polycarbonate comprising reacting allylated cyclic carbonate as shown below with thiol compound through thermal reaction in presence of catalyst at temperature ranging from ambient temperature (room temperature, RT) to 300°C or through UV reaction in presence of initiator according to the scheme given below:



wherein R = H, C1-10 alkyl, hydroxyl, C1-10 hydroxyalkyl, C3-10 alkylcarbonyl, C3-10 carbonylalkyl, C4-10 alkoxy carbonyl, C4-10 alkoxy carbonyloxy and C2-10 carboxyl group, respectively; Polythiol = alkylthiol (R₁ = C1-20 alkyl), trimethylolpropane tri(3-mercaptopropionate), glycol di(3-mercaptopropionate), glyceryl dithioglycolate, glycol dimercaptoacetate, trimethylolpropane trimer-captoacetate, pentaerythritol tetramercaptoacetate, pentaerythritol tetra(3-mercaptopropionate), or their derivatives; m=10-10000; and n=10-10000.

[Claim 8] The process as claimed in claim 1, wherein the process further comprises thermally reacting polycarbonate prepared from allylated cyclic carbonate, (meth)acrylated cyclic carbonate, or a mixture thereof with thiol compound in presence of initiator at temperature ranging from ambient temperature (room temperature, RT) to 300°C, or UV reacting polycarbonate with thiol compound in presence of initiator, thus obtaining cross linked polycarbonate or highly cross linked polycarbonate.

[Claim 9] The process as claimed in claim 7 or 8, wherein said allylated cyclic carbonate is TMPME CC, TMEME CC or a mixture thereof, and said (meth)acrylated cyclic carbonate is TMPmMA CC, TMEmMA CC, TMPmA CC, TMEmA CC or a mixture thereof.

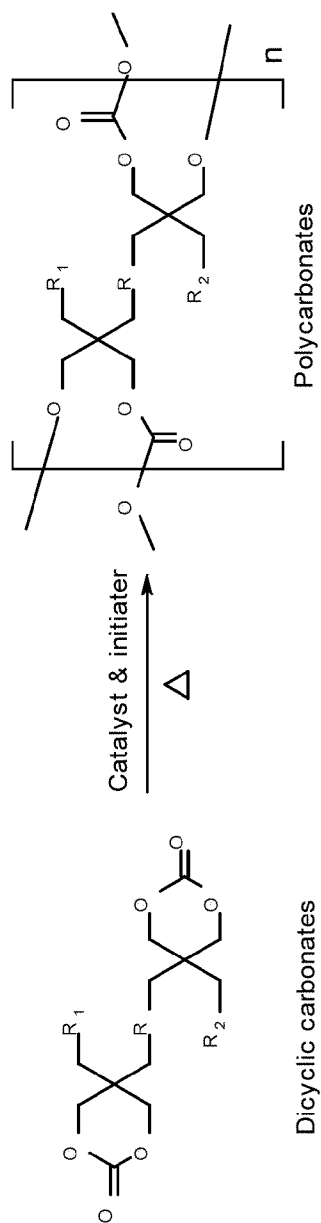
[Claim 10] A cross linked polycarbonate prepared by the process according to

claim 7 or 8.

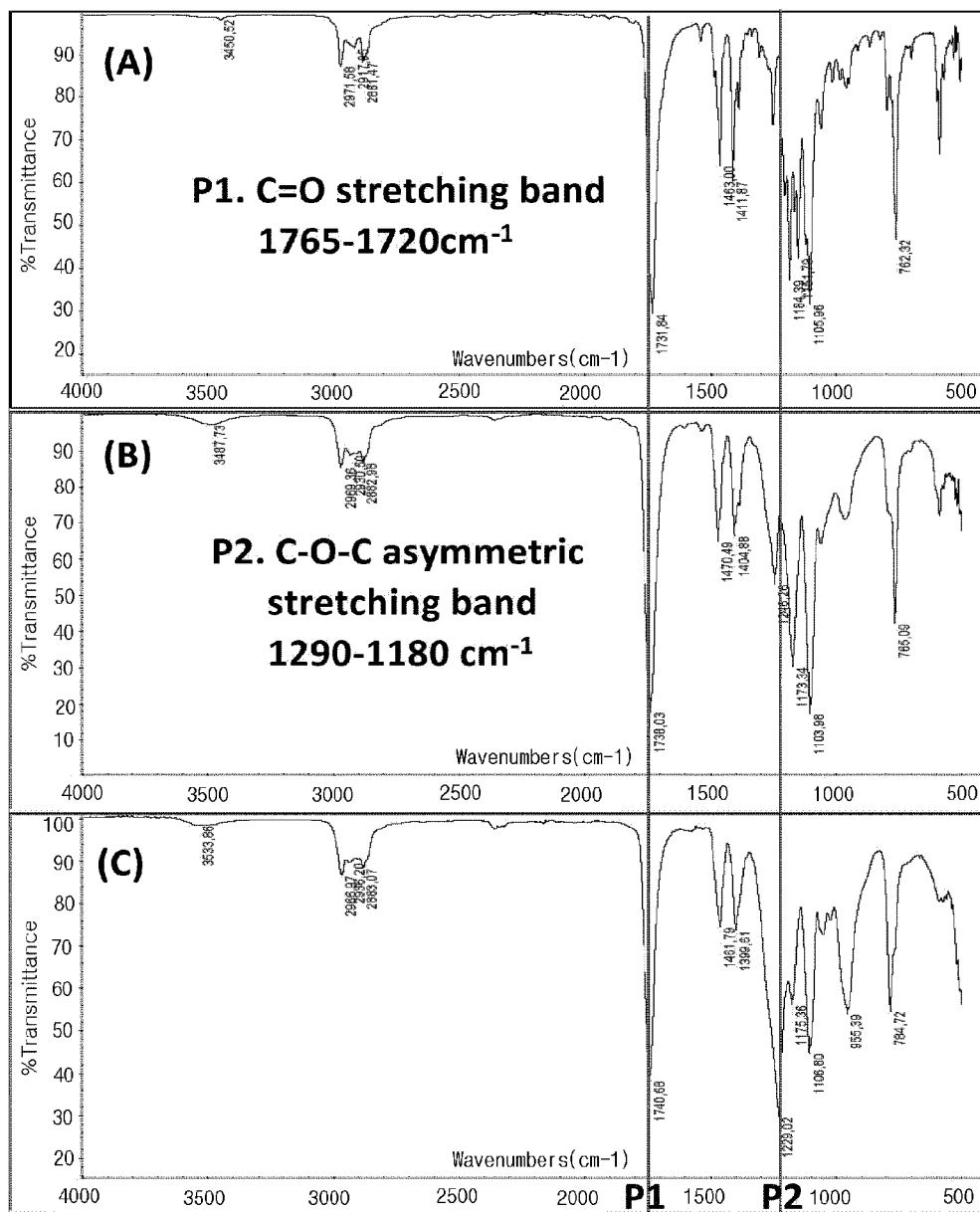
[Claim 11] The process as claimed in any one of claims 4, 7 and 8, wherein the thiol compound is chosen from dithiols, trithiols, tetrathiols, and polythiols.

[Claim 12] The process as claimed in claim 11, wherein the thiol compound is chosen from 1,2-ethylenedithiol, trimethylolpropane tris(3-mercaptopropionate), and pentaerythritol tetrakis(3-mercaptopropionate).

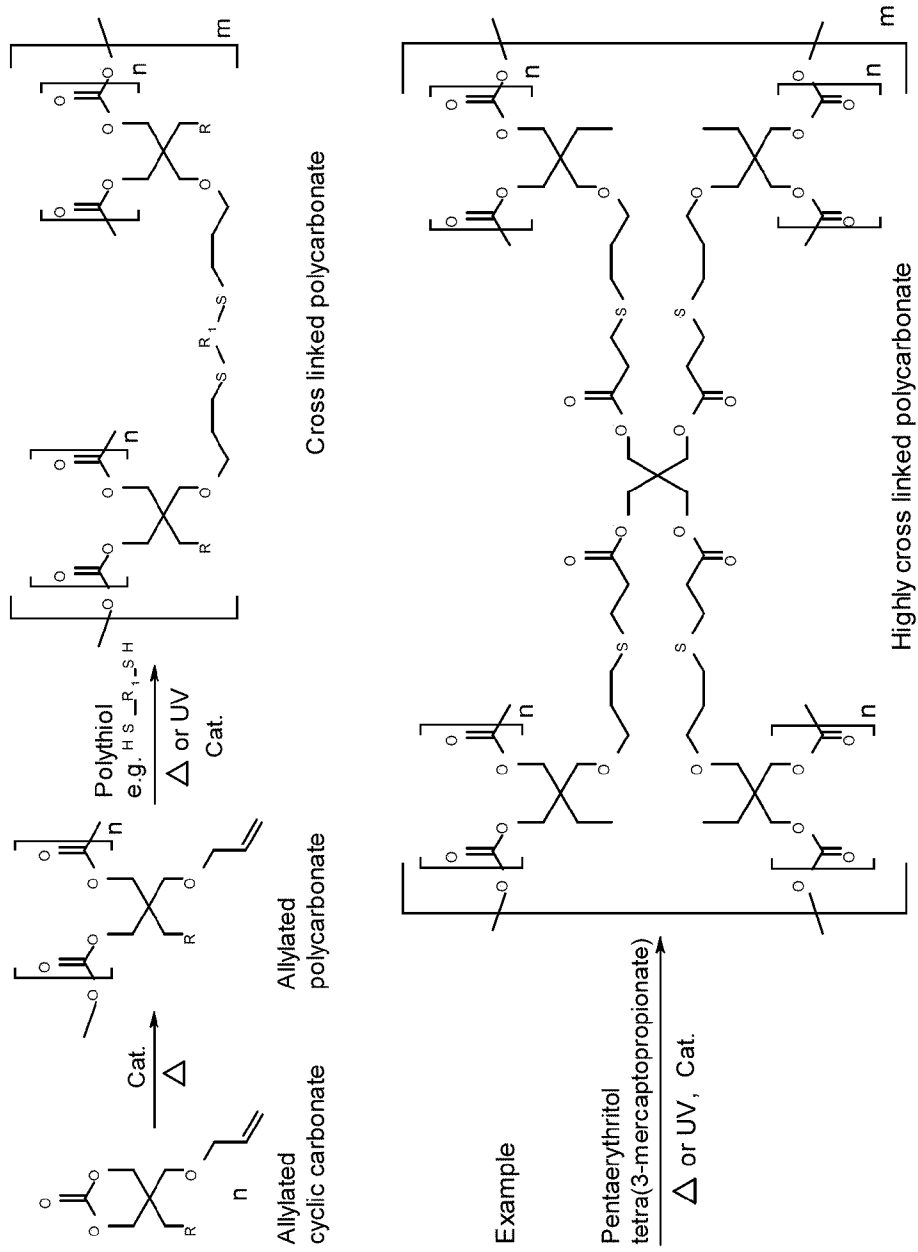
[Fig. 1]



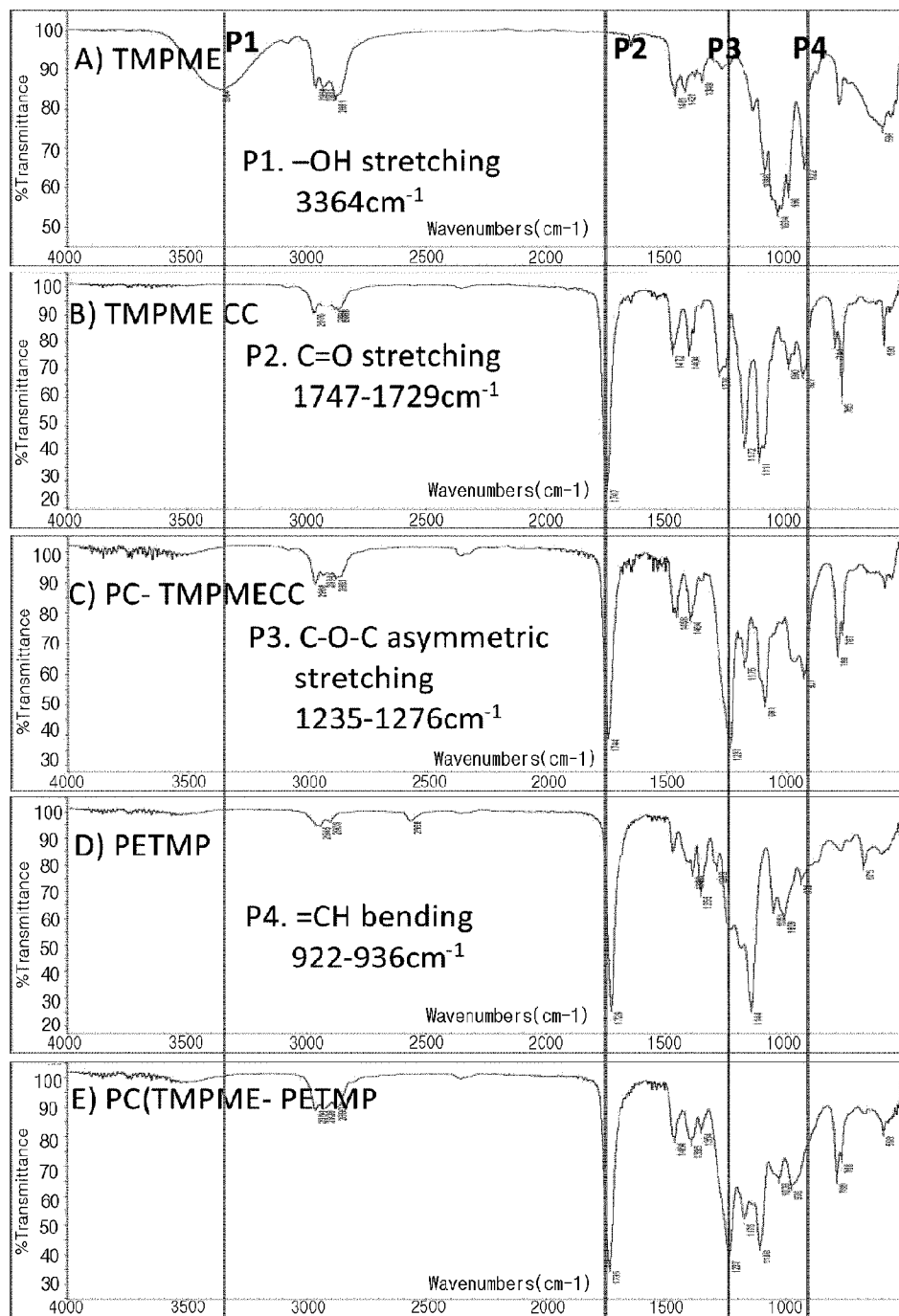
[Fig. 2]



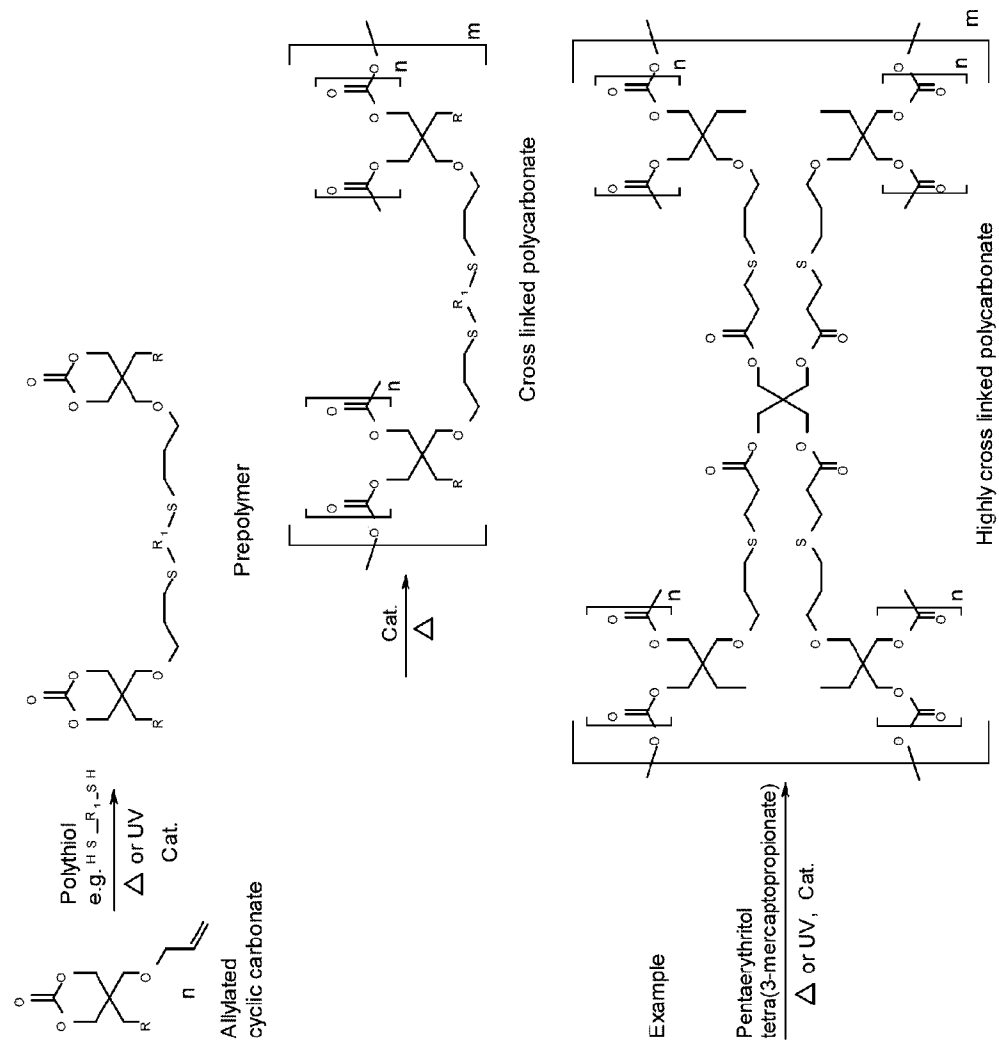
[Fig. 3]



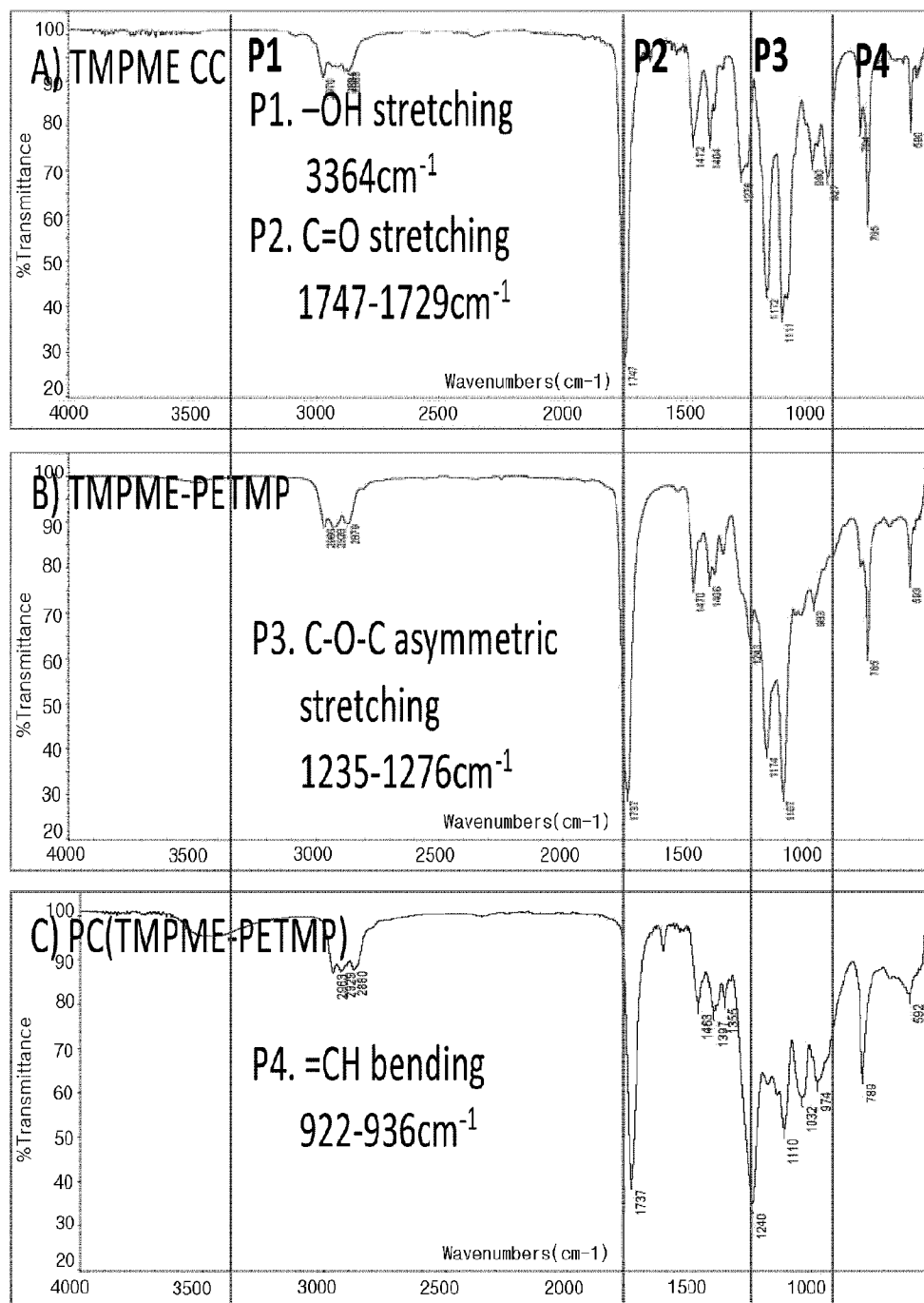
[Fig. 4]



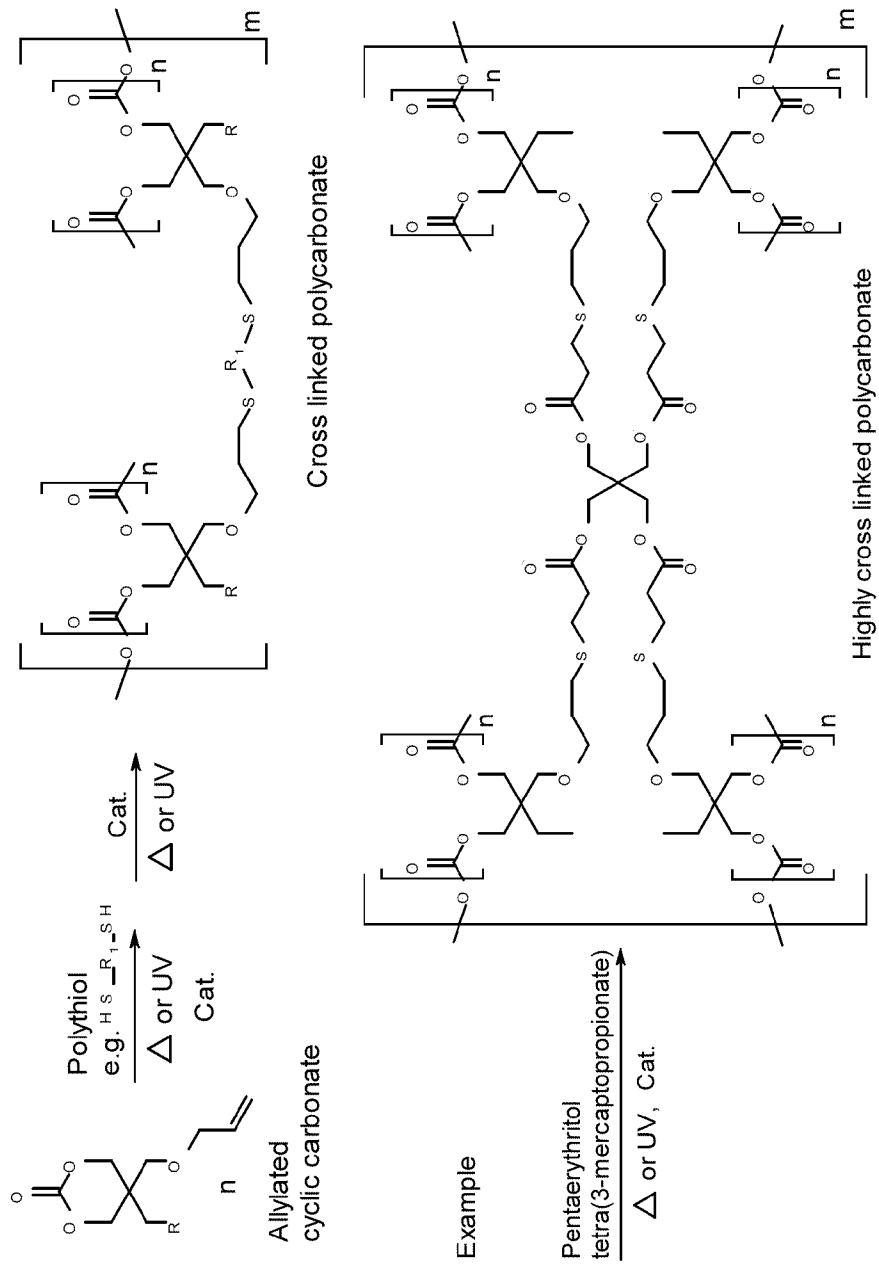
[Fig. 5]



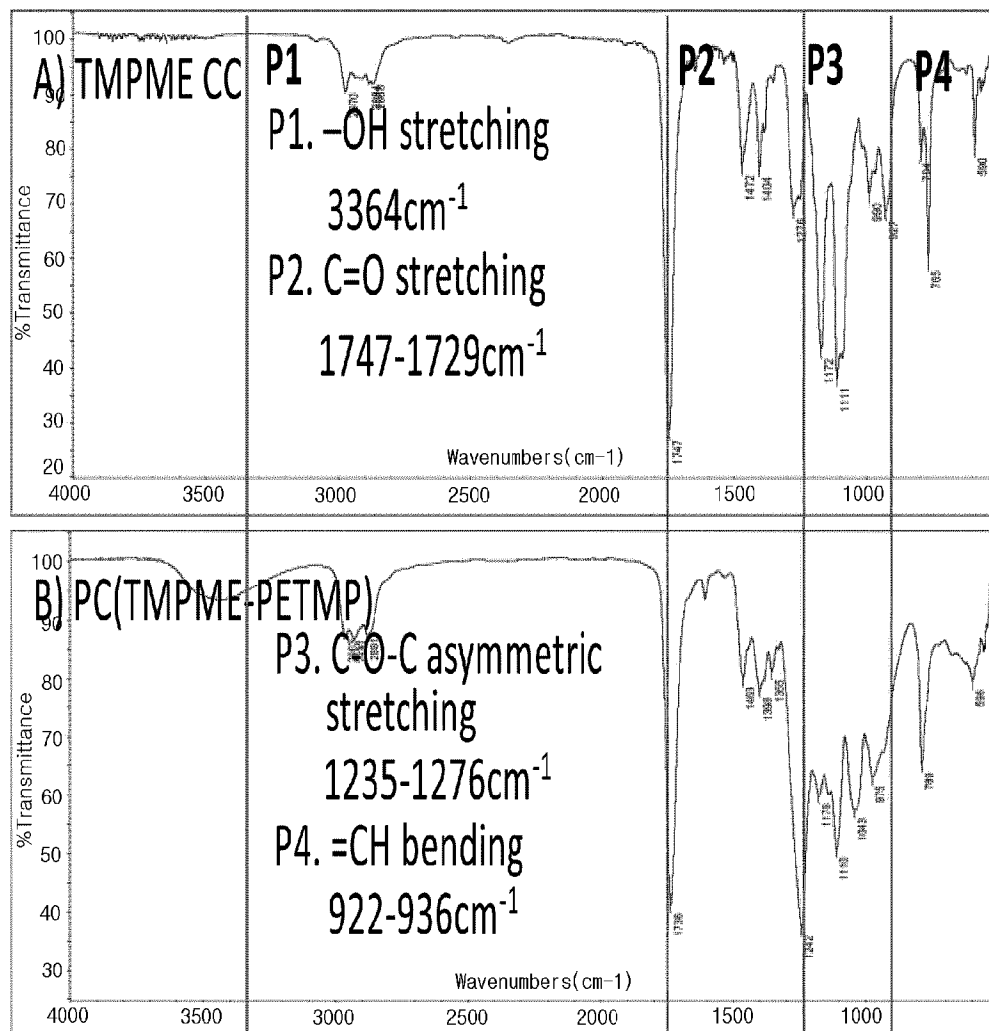
[Fig. 6]



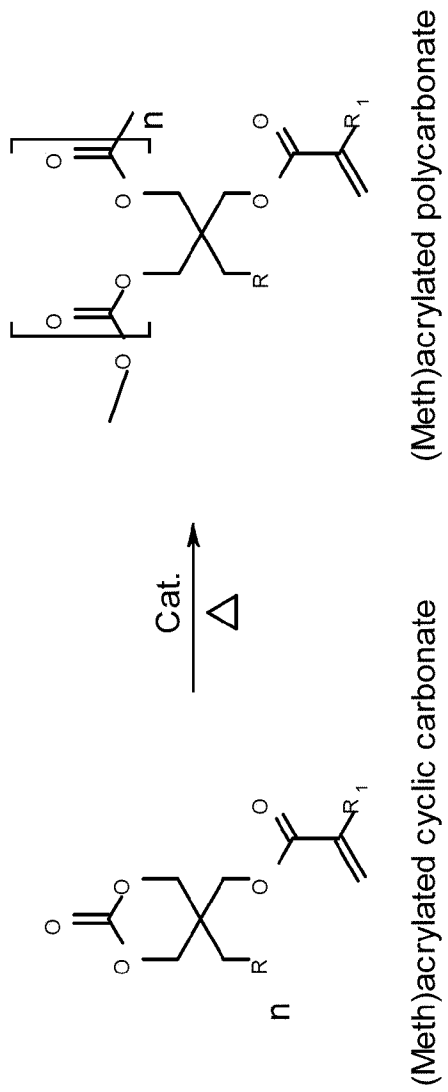
[Fig. 7]



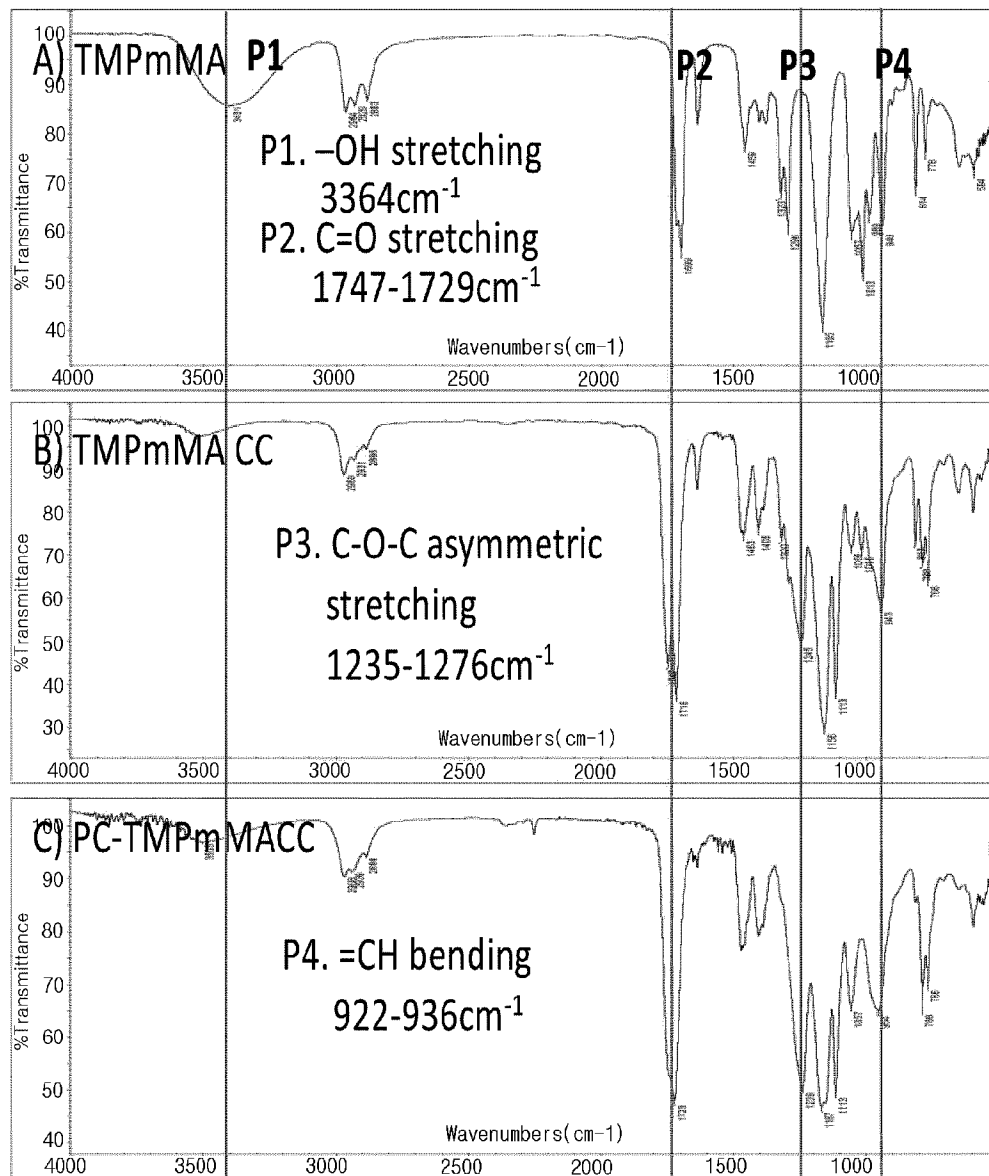
[Fig. 8]



[Fig. 9]



[Fig. 10]



[Fig. 11]

