Copper-mediated controlled radical ring-opening polymerization (RROP) of a vinylcycloalkane†

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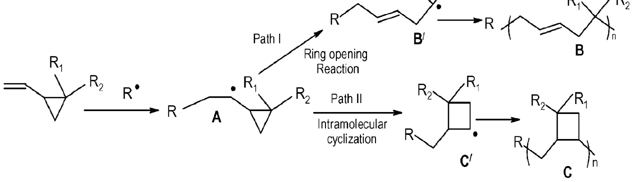
This investigation reports controlled ring-opening polymerization of a vinylcyclopropane *via* copper-mediated atom transfer radical polymerization which leads to predominantly 1,5 ring-opening polymerization.

Ring-opening polymerizations (ROP) of cyclic monomers have many interesting features and hence have been a subject of contemporary research in polymer chemistry.[1–3] ROP can introduce different functional groups in the polymer chain (such as carbon–carbon unsaturation, ether, ester *etc.*) which are difficult to achieve *via* conventional vinyl polymerization. ROP[1,4,5] can be carried out by cationic, anionic, radical, metathesis or coordination polymerization. Radical ring-opening polymerization (RROP) of vinylcyclopropanes (VCP) produces polymers containing no heteroatoms in the carbon chain backbones. Interestingly, RROP of substituted VCP leads to polymers having a carbon–carbon unsaturation and pre-designed pendant functional group separated by five carbon atoms in the repeat units. Another important characteristic feature of ROP of cyclic monomers is that it occurs with lower volume shrinkage in comparison to other polymerizations.[1–3] Conventional RROP of VCP leads to mixtures of the products obtained by ring-opening as well as *via* intramolecular cyclization reactions (Scheme 1). Controlled radical ring-opening polymerization of a vinylcycloalkane is not known so far in the literature.

In the recent advances of controlled radical polymerization[6] atom transfer radical polymerization (ATRP) is one of the most versatile synthetic tools to prepare polymers with controlled molecular weights and well-defined architecture.[7] ATRP needs an active alkyl halide as an initiator and a suitable transition metal halide (*e.g.* copper halide *etc.*) as catalyst. So far there is no documented example of application of ATRP in the radical ring-opening polymerization (RROP) of cyclic monomers. This investigation reports an example of atom transfer radical polymerization in the ring-opening polymerization (ATRROP) of a substituted vinyl cyclopropane (ECVCP) catalyzed by a copper complex. This work shows that back biting intramolecular cyclization reactions, which occur simultaneously with conventional ROP, can be suppressed to a great extent in the ATRP variant leading to polymers with desirable structure and interesting properties.

Radical ring-opening polymerization (RROP) of a substituted vinylcyclopropane (VCP) leads to several side products[2,3,5,8–11] as shown in Scheme 1. The active radical first attacks the $>C{=}C<$ to form active species of structure **A** (Scheme 1). The active radical (**A**) undergoes facile ring-opening reaction of cyclopropane to relieve ring-strain and thus forms **B**, (path I) which has $>C{=}C<$ in the main chain. Alternatively, it can undergo intramolecular cyclization to form **C** which has a cyclobutane ring in the main chain (path II in Scheme 1). Conventional radical polymerization of VCP using conventional thermal initiators (such as azobis(isobutyronitrile), AIBN or benzoyl peroxide) leads to a mixture of products of **B** and **C**.

In this investigation we have polymerized 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP) *via* ATRROP (Scheme 2) as well as *via* conventional ring-opening radical polymerization (RROP). Table 1 summarizes and compares the ring-opening polymerization (ROP) of ECVCP carried out *via* conventional free radical polymerization (FRP) and *via* ATRP. RROP of ECVCP leads to formation of an olefinic double bond ($>C{=}C<$) (due to 1,5 ring-opening polymerization) as well as the cyclobutane structure (due to intramolecular cyclization) in the main chain. Fig. 1 shows the ^{1}H NMR spectrum of poly[1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane] (PECVCP) prepared by conventional RROP of ECVCP using AIBN as an initiator. Broad resonances at δ 1.3–1.8 ppm in the ^{1}H NMR of PECVCP are attributed to the different protons inside the cyclobutane ring designated as 'e' in structure type **C** in Fig. 1. The intense peak at δ 5.2 ppm is due to the olefinic protons designated as 'd' in structure type **B** in Fig. 1. The structure types **B** and **C** are obtained *via* 1,5 ring-opening reaction and intramolecular cyclization, respectively, as shown in Scheme 1. Scheme 2 shows ATRROP of ECVCP using CuBr as catalyst in combination with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as ligand. The ^{1}H NMR of PECVCP prepared by ATRROP is shown in Fig. 2. There is an intense peak at δ 5.2 ppm indicating the



Scheme 1 Radical ring-opening polymerization (RROP) of a 1,1-disubstituted-2-vinyl cyclopropane.

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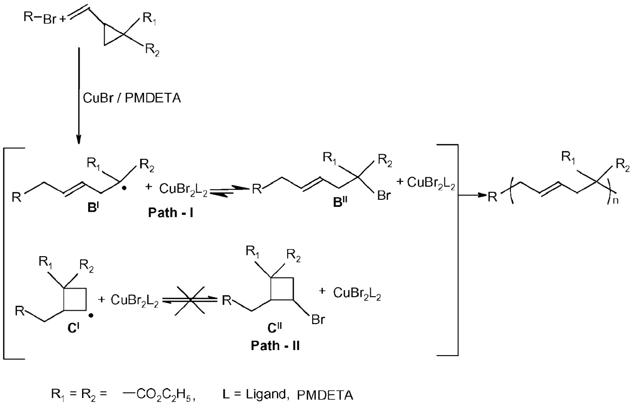

Scheme 2 Atom transfer radical ring-opening polymerization (ATRROP) of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP).

presence of olefinic protons inside the main chain. Interestingly, there is only a very small, almost insignificant resonance at δ 1.3–1.8 ppm for the protons of a cyclobutane ring. This clearly indicates that the intramolecular cyclization is largely reduced during ATRROP of ECVCP. In a controlled experiment when ECVCP was heated with CuBr/PMDETA at 90 °C, there was no polymerization. However, the same system undergoes polymerization in the presence of ethyl 2-bromoisobutyrate (EBiB) or phenylethyl bromide (PEBr) which are used as an initiator (RBr) in ATRP (Scheme 2).[6,7] The mechanism of ATRP involves a reversible dynamic equilibrium in which the instantaneous concentration of the active radicals is very low. Hence, the side reactions such as chain transfer and intramolecular cyclization are minimized. In this case PMDETA was chosen as the ligand, because it leads to faster polymerization due to lower reduction potential of the copper–PMDETA catalyst system.[6a,7d] It can be mentioned that conventional RROP of ECVCP is very slow.

The conventional RROP of ECVCP leads to very broad polydispersity index (PDI) (2.0–4.9). In the PECVCP prepared by ATRP there is large reduction in the cyclobutane ring content and the PDI is also narrow. The GPC traces of PECVCP prepared by ATRROP showed quite narrow PDI of 1.16 (see ESI† for GPC traces of this polymer), which indicates that only a single reactive species was active during the ATRROP of ECVCP, as shown in Scheme 2. The results can be explained from the stability of the active radical formed in the ATRP reaction.[7] In the case of 1,5 ring-opening reaction the active species (path-I in Scheme 2) is a tertiary radical which is more stable and is effectively stabilized by the copper catalyst. On the contrary, intramolecular cyclization leads to a secondary radical on the cyclobutane ring (path-II in Scheme 2) which is very unstable and unlikely to propagate in the ATRP reaction. ^{1}H NMR shows only a small portion of cyclobutane moiety in the polymer (Table 1). MALDI-TOF-MS (matrix assisted laser desorption ionization time of flight mass spectrometry) showed predominantly a single distribution of ions that were separated by m/z 212, the repeat mass of PECVCP. It indicates that –CO_2Et groups are not lost during the polymerization. The average M_n of PECVCP by MALDI was 2980 and PDI 1.32 which was comparable with the data obtained by GPC (ATRROP of ECVCP in Table 1) (see ESI† for MALDI-TOF-MS of PECVCP).

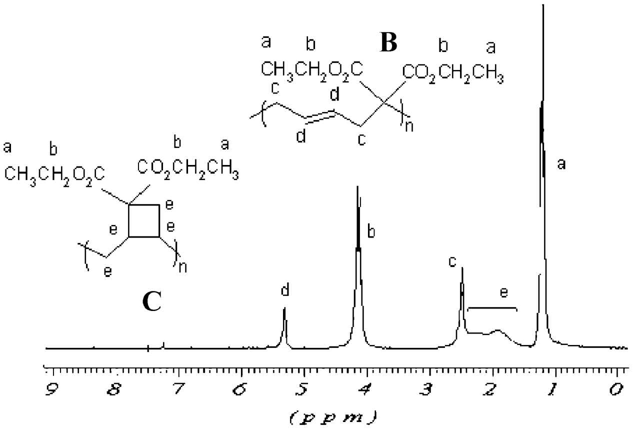

Fig. 1 ^{1}H NMR spectrum of poly(ECVCP) prepared by RROP using AIBN initiator.

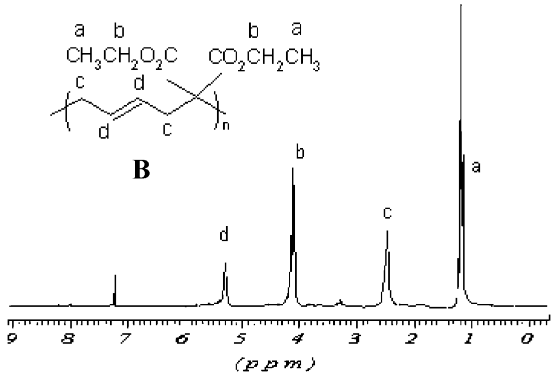

Fig. 2 ^{1}H NMR spectrum of poly(ECVCP) prepared by ATRROP.

The chemical structure of the resulting PECVCP has an interesting impact on the glass transition temperature (T_g) of the polymer. DSC analysis shows that the PECVCP prepared by conventional RROP has T_g of 24 °C, whereas PECVCP

Table 1 Radical ring-opening polymerization (RROP) of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP) using ATRP and conventional free radical polymerization (FRP)

Entry	Type of polymerization	Catalyst system	Yield (%)	M_n^e/g mol^{-1}	PDI	Cyclobutane in main chain (%)
1	ATRROP[a]	[c]PEBr/CuBr/PMDETA	20	2329	1.22	1.2
2	ATRROP[a]	[d]EBiB/CuBr/PMDETA	33	3033	1.16	1.3
3	RROP[a]	AIBN	33	8300	2.0	36
4	RROP[b]	AIBN	65	13 200	4.9	33

[a] Solution polymerization. [b] Bulk polymerization. [c] Phenyl ethyl bromide (PEBr) as initiator. [d] Ethyl 2-bromoisobutyrate (EBiB) as initiator. [e] Molecular weight calculated w.r.t. polystyrene standard.

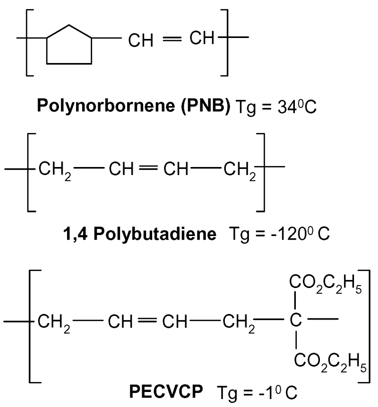

Fig. 3 Chemical structure and T_g of few relevant polymers.

prepared by ATRROP has a T_g of −1 °C (see ESI† for the DSC traces of PECVCP prepared by RROP and ATRROP). The higher T_g of PECVCP prepared by RROP compared to that prepared by ATRROP is due to the restriction in main chain rotation, because of the presence of cyclobutane rings in the main chain. It is known that restriction in rotation around the main chain increases T_g of the polymer.[4] For example, polynorbornene (PNB) which is prepared by ring-opening metathesis polymerization (ROMP) has cyclopentyl rings in the main chain and has a T_g of 34 °C,[12] whereas polybutadiene itself has a very low T_g of −120 °C.[12] The chemical structure of PECVCP prepared by ATRROP is somewhat similar to 1,4-polybutadiene, but with two $-CO_2C_2H_5$ groups at the β position with reference to the $>C{=}C<$ bond (Fig. 3). Hence, PECVCP has a higher T_g than polybutadiene.

In conclusion, this communication shows an example of the application of ATRP in the ring-opening polymerization (ATRROP) of ECVCP, a substituted vinylcyclopropane. The ATRROP of VCP leads to predominantly 1,5 ring-opening polymerization leading to a linear polymer having $>C{=}C<$ in the backbone. The different side reactions such as intramolecular cyclizations are greatly suppressed during the ATRROP. Interestingly, with relatively lower T_g with two ester groups in each repeating unit this polymer can be a potential polar elastomer.

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