Synthesis of Poly(alkyl alkynoates) from Diynes, CO_2, and Alkyl Dihalides by a Copper(I) Salt Catalyst

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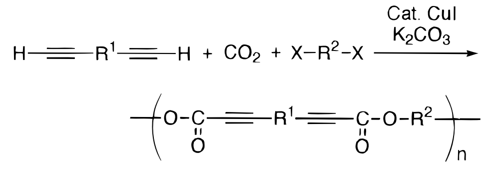
Polymer synthesis using CO_2 has attracted increasing interest stemming from a need for a potential alternate carbon source to petroleum as well as the environmental concern about increasing concentration of CO_2 in the atmosphere. However, only a few examples of CO_2 copolymerization are known. Inoue et al. reported an alternating copolymerization of CO_2 and epoxide to yield an aliphatic polycarbonate, the first example of a polymer synthesis directly from CO_2.[1] Soga et al.[2] and Rokicki et al.[3] reported independently the syntheses of polycarbonates by reaction of CO_2, alkali metal diolates, and alkyl dihalides in the presence of crown ether. Tsuda et al. reported an alternating copolymerization of CO_2 and 2,6-octadiyne to yield poly(2-pyrone), the first example of copolymerization of CO_2 with $C(CO_2)-C$ bond formation.[4] We previously reported a one-pot synthesis of completely alternate polycarbonate from CO_2, diols, and alkyl dihalides.[5] Recently, during the course of our studies directed toward the effective utilization of CO_2, we found a novel catalytic reaction for the synthesis of alkyl alkynoates from 1-alkynes, CO_2, and alkyl halides mediated by copper(I) salt in the presence of K_2CO_3.[6] In this communication, we wish to report a convenient synthesis of poly(alkyl alkynoates) from CO_2 applying this method (Scheme 1).

Scheme 1



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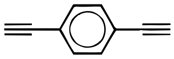
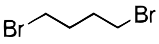
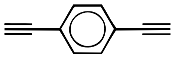
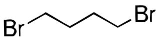
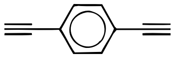
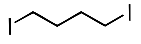
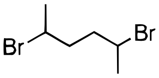
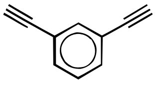
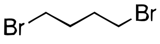
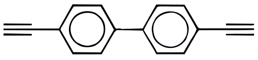
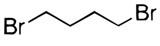
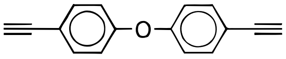
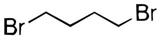
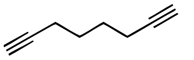
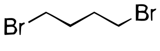
Typically, a mixture of 1,4-diethynylbenzene (0.252 g, 2.00 mmol), 1,4-dibromobutane (0.432 g, 2.00 mmol), CuI (0.030 g, 0.160 mmol), and anhydrous K_2CO_3 (1.67 g, 12.0 mmol) in *N*,*N*-dimethylacetamide (DMAc, 6 cm^3) was agitated at 80 °C for 24 h under an atmosphere of CO_2. After the reaction, DMAc (50 cm^3) was added to the reaction mixture and the solid was filtered off. Then the filtrate was poured into methanol with stirring to give a precipitate, which was washed successively with water (50 cm^3), 1 N HCl aq (50 cm^3), water (50 cm^3), and methanol (50 cm^3). This procedure afforded 0.438 g of polymer.[7] Results are summarized in Table 1. In all cases, alternate copolymerization of CO_2, diyne, and alkyl dihalide was effected and poly(alkyl alkynoate) was obtained.

The IR spectrum of the polymer obtained from 1,4-diethynylbenzene and 1,4-dibromobutane displayed strong absorption peaks at 1705, 1285, and 1185 cm^{-1} attributable to the stretching of the carbonyl, oxycarbonyl, and alkoxy groups of the linear ester linkage, respectively, and at 2205 cm^{-1} attributable to the stretching of the carbon−carbon triple bond of the conjugated alkyne. The ^1H-NMR spectrum exhibited broad peaks at δ 7.59, 4.31, and 1.87 with the same intensity ratio, assignable to aromatic protons and

Table 1. Poly(alkyl alkynoates) 1 from CO_2, Diynes, and Alkyl Halides[a]

Run	$\equiv-R^1-\equiv$	$X-R^2-X$	Catalyst	Time (h)	Yield (%)[b]	*Mn*[c]	*Mw/Mn*[c]
1			CuI	24	82	6000	5.12
2			CuI+2phen	8	77	6200	5.66
3			CuI+2phen	8	34	3300	2.51
4			CuI+2phen	8	11	1000	2.36
5			CuI	24	66	8400	4.82
6			CuI	24	61	4400	2.92
7			CuI	24	81	6500	3.02
8			CuI	24	9	5200	1.99

[a] The polymerization was carried out in the presence of catalyst (4 mol %) and K_2CO_3 at 80 °C under an atmosphere of CO_2. [b] Polymer insoluble in methanol. [c] Number-average molecular weight M_n and molecular weight distribution M_w/M_n estimated by gel-permeation chromatography with chloroform as eluent (based on polystyrene standards).

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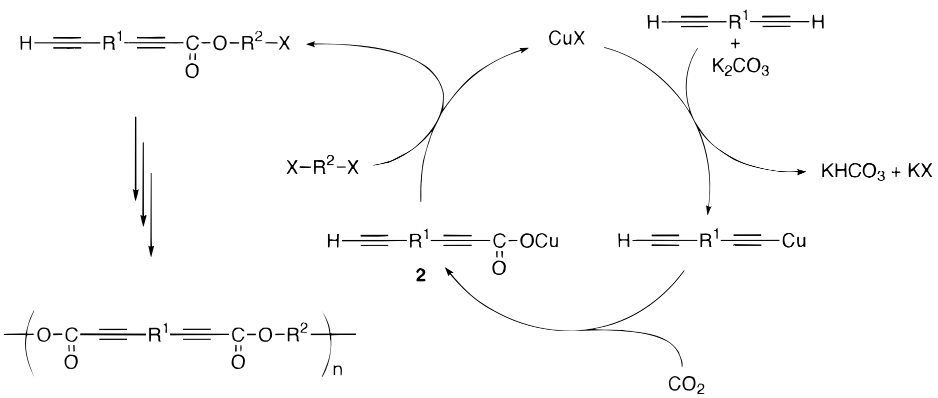
Scheme 2



methylene protons at the α- and β-positions of the ester linkage, respectively. The $^{13}C\{^1H\}$-NMR spectrum exhibited peaks at δ 153.5 assignable to the carbonyl carbon, δ 132.9 and 121.7 assignable to aromatic carbons, δ 84.7 and 82.7 assignable to acetylene carbons, and δ 65.5 and 25.0 assignable to methylene carbons. The C and H elemental analysis values were in accord with those for poly(alkyl alkynoate). These results and the mechanistic investigation of this method[6] indicate that, the polymer obtained from CO_2, 1,4-diethynylbenzene, and 1,4-dibromobutane is poly(alkyl alkynoate), poly[oxycarbonylethynylene-1,4-phenyleneethynylenecarbonyloxybutylene] (**1**).

Inorganic bases such as K_2CO_3 which do not react readily with alkyl dihalide are suited for this reaction, because organic bases such as tertiary amines suffer from *N*-alkylation with alkyl dihalide. Polar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), DMAc, and *N*-methyl-2-pyrrolidone (NMP) were suitable for this polymerization. The reaction was heterogeneous even with these polar solvents. Among these solvents, the maximum yield (82%) and the highest number-average molecular weight M_n (6000) were obtained in DMAc when 1,4-diethynylbenzene and 1,4-dibromobutane were used as the substrates (run 1). Addition of 1,10-phenanthroline (phen) as a ligand of CuI accelerated the polymerization, affording the polyester in a comparable yield and number-average molecular weight to those in run 1 in a shorter reaction time (run 2). The yield of the polyester declined considerably with primary aliphatic diiodide or secondary aliphatic dibromide (runs 3 and 4). The polymerization with several aromatic diynes, CO_2, and 1,4-dibromobutane proceeded efficiently to afford polyesters in good yields (runs 5−7); however, that with an aliphatic diyne, i.e., 1,7-octadiyne, was sluggish, affording only a small amount of polyester (9% yield, run 8).

This polymerization is conjectured to proceed according to Scheme 2. Diyne and CuI afford copper acetylide in the presence of K_2CO_3, which in turn reacts with CO_2 to form copper carboxylate (**2**).[8] **2** thus formed reacts with alkyl dihalide to produce an ester linkage, and copper salt is regenerated.[6] As a result of the sequence of these reactions, poly(alkyl alkynoate) is produced. The key for this reaction is nucleophilic attack of **2** on alkyl dihalide with simultaneous regeneration of copper salt, thus making the reaction catalytic as a whole. Polar aprotic solvents surely promote this nucleophilic substitution step. Addition of phen as a ligand which increases the electronic density of the copper compound may accelerate both the nucleophilic addition of copper acetylide to CO_2 and the nucleophilic substitution of **2** to alkyl dihalide.

The procedure described here offers a convenient synthesis of poly(alkyl alkynoates) from easily accessible starting materials.

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References and Notes

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(6) Fukue, Y.; Oi, S.; Inoue, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2091.
(7) IR (KBr): 2205, 1705, 1285, 1185 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 7.59 (br), 4.31 (br), 1.87 (br). Intensity ratio: 4:4:4. $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 153.5, 132.9, 121.7, 84.7, 82.7, 65.5, 25.0. Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 72.06; H, 4.81. The average molecular weight and molecular weight distribution of polymers were measured by GPC (polystyrene standards).
(8) Tsuda, T.; Ueda, K.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1974**, 380.

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