Fixing Carbon Dioxide Concurrently with Radical Polymerization for Utilizing Carbon Dioxide by Low-Energy Cost

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Introduction

Carbon dioxide is an abundant nonpetroleum resource, and its efficient transformation into organic materials is one of the best solutions for saving the use of petroleum resources.[1−6] However, typical reactions of carbon dioxide require high energy, for example, high temperature or high pressure, because of the stability of carbon dioxide. The reaction of carbon dioxide and epoxides that afford five-membered cyclic carbonates proceeds smoothly under relatively mild conditions.[7−14] Although this reaction is effective in the preparation of monomers or in polymer reactions, these reactions are not suitable enough to save the energy to transform carbon dioxide by the multiple steps required.[15−30] For example, the most-examined polymers bearing five-membered cyclic carbonate are polymethacrylates prepared from two-step methods: radical polymerization of a methacrylate bearing cyclic carbonate moieties (DOMA) prepared from the reactions of carbon dioxide and glycidyl methacrylate (GMA) and reactions of carbon dioxide and polyGMA obtained by radical polymerizations. In addition to the two steps, including the required purification processes, these reactions are time-consuming (total time >10 h). Accordingly, we attempted a one-step reaction consisting of radical polymerization and paralleled carbon dioxide fixation.

Results and Discussion

Radical Polymerization of Glycidyl Methacrylate Paralleled with Carbon Dioxide Fixation. We employed LiBr for this combined reaction because of its high activity in *N*-methyl pyrrolidinone (NMP).[8] The radical polymerization of GMA was conducted under a carbon dioxide atmosphere (1 atm) in the presence of LiBr and 2,2-azobisisobutyronitrile (AIBN) (3.0 mol % with respect to GMA) in NMP, *N*,*N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and 1,4-dioxane (DOX) (Table 1, runs 1−4). Polar solvents, especially amides, were effective for higher efficiency of the transformation into the carbonate group in a similar manner with the reaction of polyGMA with carbon dioxide.[16,31] The almost quantitative carbon dioxide incorporation and the quantitative yield within 5 h at 80 °C (run 1) are significantly advantageous over the reported polymer reaction of polyGMA with carbon dioxide using higher amounts of catalysts (e.g., 2 h at 100 °C using 10 mol % catalysts)[15,19] after the preparation of polyGMA (e.g., several hours at 60 °C[33,34] or 4 h at 75 °C[35])[19] and the polymerization of DOMA, whose preparation requires time and care to prevent spontaneous polymerization affording insoluble products.[16] The negligible fixation of carbon dioxide in DOX originates from the very poor solubility of LiBr in DOX (run 4). When the reaction was conducted at lower temperatures (runs 5−7), both the carbon dioxide incorporation ratios and the yields became lower, whereas the decrease in the carbon dioxide incorporation ratios is more obvious. A probable reason is the slower incorporation of carbon dioxide into polymers than into GMA, originating from the formation of polymers bearing many oxirane groups via the polymerization being much faster than carbon dioxide fixation. The higher molecular weights in the polymerizations at lower temperatures can be ascribed to the lower frequency of the chain transfer reaction to the carbonate group.[16] The carbonation degrees can also be controlled by the amount of LiBr (runs 8 and 9), and the quantitative conversion of the oxirane to the carbonate ring was attained using a 5 mol % amount of LiBr. The use of benzoyl peroxide (BPO) was not effective for this reaction (runs 10 and 11). Despite the high carbon dioxide incorporation efficiency, the yields were low because of the low conversions of the double bond moieties. We attributed this unsuccessful result to some side reactions between the oxy radical and LiBr, considering the fact that the polymerization mixture turned red during the polymerization.

Table 1. Radical Polymerization of GMA Paralleled with Carbon Dioxide Fixation[a,b]

run	temp (°C)	initiator	LiBr (mol %)	solvent	conv. of C=C[c]	copolymer composition (*x*/*y*)[c,d]	yield (%)[e]	M_n (M_w/M_n)[f]
1	80	AIBN	3	NMP	<99	98/2	95	22 300 (1.94)
2	80	AIBN	3	DMF	<99	87/13	76	10 400 (3.09)
3	80	AIBN	3	DMSO	98	55/45	85	15 500 (3.31)
4	80	AIBN	3	DOX	99	0/100	83	14 600 (2.05)
5	50	AIBN	3	NMP	76	45/55	73	105 700 (2.22)
6	60	AIBN	3	NMP	96	76/24	90	39 800 (3.68)
7	70	AIBN	3	NMP	<99	85/15	95	25 900 (2.81)
8	80	AIBN	0.5	NMP	<99	33/67	96	18 400 (2.84)
9	80	AIBN	5	NMP	<99	100/0	96	10 700 (3.79)
10	80	BPO	3	NMP	56	91/9	54	33 700 (4.10)
11	90	BPO	3	NMP	58	100/0	58	12 200 (3.79)

[a] Reaction conditions: CO_2 (1 atm), GMA (1.00 mmol), initiator: 3 mol %, LiBr, solvent (0.50 mL), 5 h. [b] AIBN: 2,2′-azobisisobutyronitrile, BPO: benzoyl peroxide, NMP: *N*-methyl pyrrolidinone, DMF: *N*,*N*-dimethyl formamide, DMSO: dimethyl sulfoxide, DOX: 1,4-dioxane. [c] Determined by ^{1}H NMR spectroscopy. [d] The ratio, *x* and *y*, indicates the composition of the carbonate and oxirane units, respectively. [e] Isolated yield after precipitation with methanol. [f] Estimated by SEC (DMF containing 10 mM LiBr, polystyrene standard).

Scheme 1. Radical Polymerization of GMA Paralleled with Carbon Dioxide Fixation

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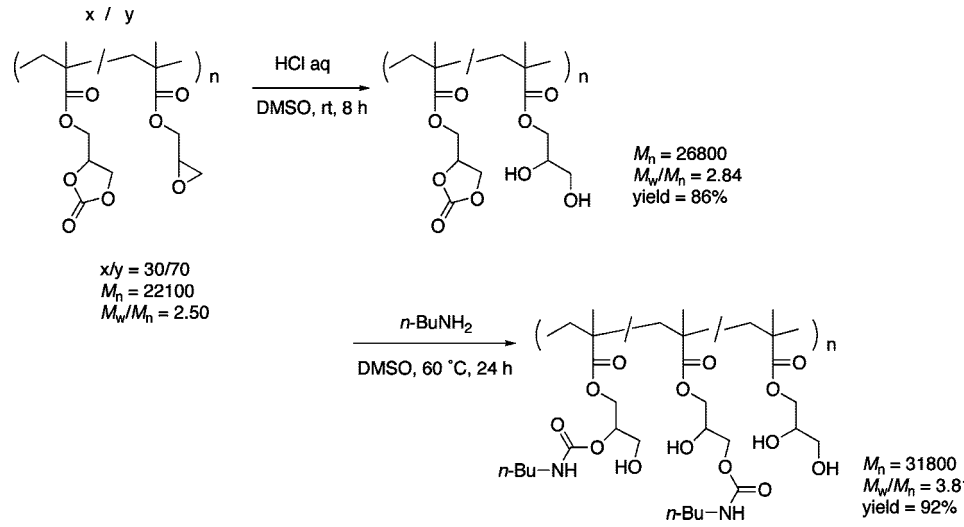
Scheme 2. Transformation of Poly(DOMA-*co*-GMA) by Aminolysis of Carbonate Moieties Followed by Hydrolysis of Oxirane Moieties



We transformed both the cyclic carbonate and the oxirane moieties in the polymer separately (Scheme 2). As a model for enzyme immobilization materials and aqueous paints, we prepared a hydrophilic polymer bearing carbonate moieties, which can react with amines.[16] The polymer with the composition of carbonate/oxirane = 30/70 (M_n = 22 100 and M_w/M_n = 2.50) was employed. First, the oxirane groups were hydrolyzed by treatment with aqueous HCl at room temperature in DMSO. The quantitative conversion to the diol groups was confirmed by NMR spectrometry, and the hydrolysis of the carbonate group was not detectable (see the Supporting Information). Then, the carbonate groups were reacted with *n*-butylamine and were transformed into hydroxyurethane moieties quantitatively. The solubility of the polymer after the hydrolysis is almost identical to the prepolymer (e.g., soluble in THF and DMSO), whereas the polymer after the aminolysis became soluble in water and methanol. When the aminolysis was conducted before the hydrolysis, the resulting polymer was insoluble because of the cross-linking reaction by the reaction of oxirane groups and primary amines, which was followed by the reaction of the resulting secondary amines with oxirane groups.

Conclusions

This note described a facile synthesis of carbonate-containing polymers by radical polymerization of GMA paralleled with carbon dioxide fixation into the oxirane moieties. This combined reaction requires shorter time for quantitative polymerization and carbon dioxide fixation than conventional methods in which the polymerization and carbon dioxide fixation are separately conducted. The important advantage of this reaction is using the energy of polymerization for carbon dioxide fixation, by which carbon dioxide serves as a resource for polymers with a very low-energy cost. The carbonation degree could be controlled by the choice of reaction conditions, and the remained oxirane moieties and the resulting carbonate moieties could be separately transformed. Owing to the specific reactive groups, the polymers are potentially applicable as paints, adhesives, and so forth.

Supporting Information Available: Experimental procedures and NMR spectra of polymers after hydrolysis and aminolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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