for stimulating discussions, and to J. W. Kennedy for making the manuscript of ref 5 available prior to publication.

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Synthesis of Polyether–Polycarbonate Block Copolymer from Carbon Dioxide and Epoxide Using a Metalloporphyrin Catalyst System

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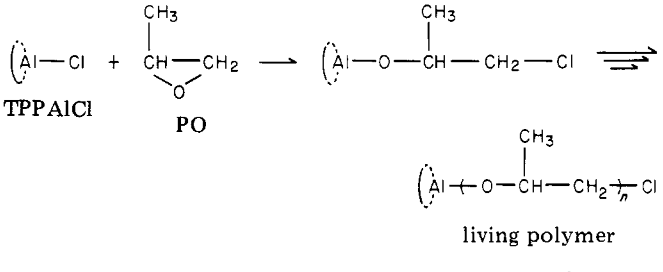
Chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization.[1] We have studied in detail the alternating copolymerization of carbon dioxide and epoxide, mainly by using a diethylzinc-based system, to give polycarbonates of high molecular weight[2] but very broad molecular weight distribution.

Recently, we found that the reaction product between equimolar amounts of some porphyrins and diethylaluminum chloride ((porphinato)aluminum chloride) caused very effectively the living polymerization of epoxides to give homopolyethers and block polyethers of controlled molecular weight.[3-5] The structure of the propagating end was demonstrated to be a (porphinato)aluminum alkoxide, formed by the insertion of epoxides into the Al–Cl bond of the catalyst;[6] for example



This paper reports the possibility of the copolymerization of carbon dioxide and propylene oxide initiated by this alkoxide, a living polyether, for the purpose of synthesizing polyether–polycarbonate type block copolymers with narrow molecular weight distributions.

Experimental Methods

Propylene oxide and dichloromethane were purified by the previously described method.[3] Dioxane was purified by bubbling nitrogen gas through a mixture of commercial dioxane and dilute hydrochloric acid, washing with an aqueous solution of potassium hydroxide, and distilling first over potassium hydroxide and then over metallic sodium under nitrogen. Commercial high-purity carbon dioxide was dried by passing it through a column packed with molecular sieve and then through a column packed with phosphorus pentoxide.

Preparation of the Catalyst. Equimolar amounts of 5,10,15,20-tetraphenylporphine ($TPPH_2$) and diethylaluminum chloride were used and allowed to react as described before.[3] Polymerization of propylene oxide, for preparation of "living" prepolymer, was carried out in dichloromethane at room temperature in a glass ampule at a monomer-to-catalyst ratio of 30 (0.03 mol (1.74 g) of propylene oxide) or 60 (0.06 mol (3.48 g) of propylene oxide). After the monomer was completely polymerized, the volatile materials were removed under reduced pressure, and then dichloromethane or dioxane was added to the residue, the living prepolymer of propylene oxide, which was then used in the next step.

For the block copolymerization, measured amounts of carbon dioxide and propylene oxide were charged into the ampule containing the living prepolymer solution and cooled with liquid nitrogen. Then this ampule was sealed under reduced pressure, and the reaction mixture was stirred at room temperature. Copolymerization under a CO_2 pressure of 50 kg·cm^{-2} was carried out in a stainless steel autoclave. After a period of 15 or 40 days the volatile materials were removed from the reaction mixture under reduced pressure, and the resulting product was dissolved in benzene and freeze-dried in vacuo.

Average molecular weight and molecular weight distribution of the prepolymer and of the final product were evaluated by gel permeation chromatography (GPC) on the basis of calibration curves obtained by using standard poly(ethylene oxides) for the high molecular weight region and standard poly(propylene glycols) for the lower molecular weight region. Standard poly(ethylene oxides) were obtained from Toyo Soda Manufacturing Co., Ltd.: $\bar{M}_n = 22\,000$ ($\bar{M}_w/\bar{M}_n = 1.14$), $\bar{M}_n = 39\,000$ ($\bar{M}_w/\bar{M}_n = 1.03$), and $\bar{M}_n = 72\,000$ ($\bar{M}_w/\bar{M}_n = 1.02$). Standard poly(propylene glycols) were obtained from Lion Fat and Oil Co., Ltd.: $\bar{M}_n = 1000$ and $\bar{M}_n = 2000$ ($\bar{M}_w/\bar{M}_n \approx 1$). The GPC measurements were performed on a Toyo Soda Model HLC-802UR gel permeation chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent. The content of oxycarbonyl units in the final product was calculated from the ^{1}H NMR signals of methine and methylene protons next to the ether linkages (δ 3.2–3.7) and to the carbonate linkages (δ 3.9–4.9). Signals due to propylene carbonate, which was detected in trace amounts in the infrared spectrum, were negligible in the ^{1}H NMR spectrum.

Results and Discussion

The results of the block copolymerization and the characterization of the prepolymer and of the final product are summarized in Table I.

Figure 1 illustrates the GPC profiles of the prepolymer and the final product (runs 1 and 4). In each case, the final product showed a unimodal and sharp elution curve in a higher molecular weight region relative to that of the prepolymer used, with a ratio of weight-average molecular weight to number-average molecular weight ($\bar{M}_w/\bar{M}_n$) of 1.1–1.2. This result clearly indicates the absence of prepolymer in the final product.

Furthermore, all of the final products showed infrared absorption bands attributable to linear carbonate linkages (1740, 1260 cm^{-1}) (Figure 2). Considering the absence of the prepolymer in the final product, this result confirms that copolymerization of carbon dioxide and epoxide ac-

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Table I
Copolymerization of Carbon Dioxide and Propylene Oxide (PO) with Living Poly(propylene oxide) as Prepolymer[a]

	prepolymer			copolymerization				final product			
run	prepolymer used, g	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	solvent, mL	time, days	charged PO, g	CO_2 pressure, $kg \cdot cm^{-2}$	yield, g	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$f_{CO_2,block}$, mol %
1	3.2	3100	1.08	40	40	11.6	8	6.4	5600	1.11	22
2	1.3	1200	1.09	30	15	17.4	50	6.8	5100	1.18	32
3	1.4	1500	1.07	30[b]	15	17.4	8	7.4	6700	1.10	e
4[c]	1.4	1200	1.08	20	15	17.4	8	11.5	9000	1.22	e
5[d]	1.4	1200	1.09	20	15	17.4	8	7.3	6200	1.18	e

[a] In dichloromethane at room temperature in diffused light. [b] In dioxane. [c] In visible light (xenon lamp); irradiation time = 71 h. [d] In the dark. [e] Considered to have an oxycarbonyl content of about 20 mol % from the IR spectrum.

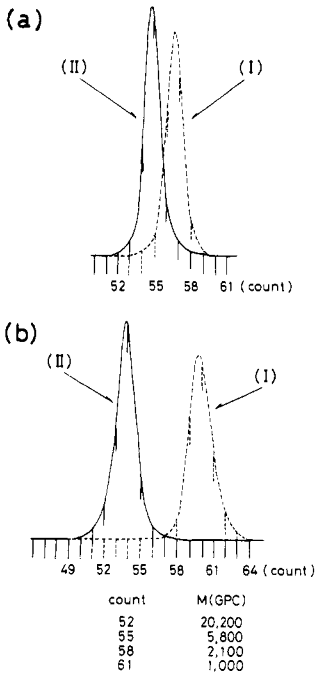


Figure 1. GPC profiles of the copolymerization of carbon dioxide and propylene oxide with living poly(propylene oxide): (a) run 1 in Table I; (b) run 4 in Table I. I, prepolymer of propylene oxide; II, final product.

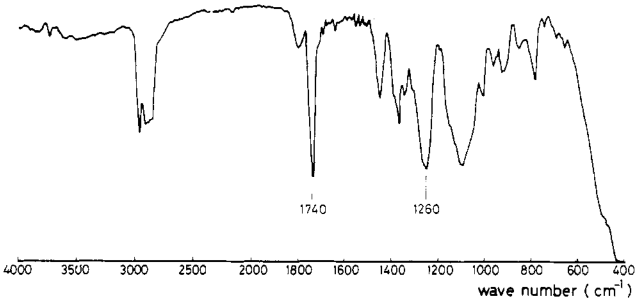
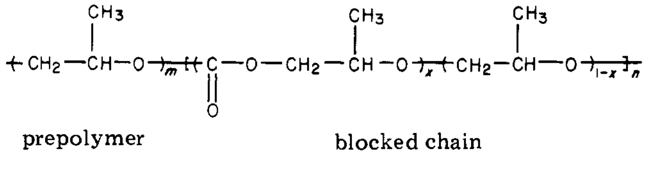


Figure 2. Copolymerization of carbon dioxide and propylene oxide with living poly(propylene oxide). IR spectrum of the final product (run 2 in Table I).

tually took place from the propagating end of the epoxide polymerization to form a polyether–polycarbonate type block copolymer:



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}H-O\right)_m\!\left[\left(\underset{\underset{\displaystyle O}{\|}}{C}-O-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}H-O\right)_x\!\left(CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}H-O\right)_{1-x}\right]_n$$

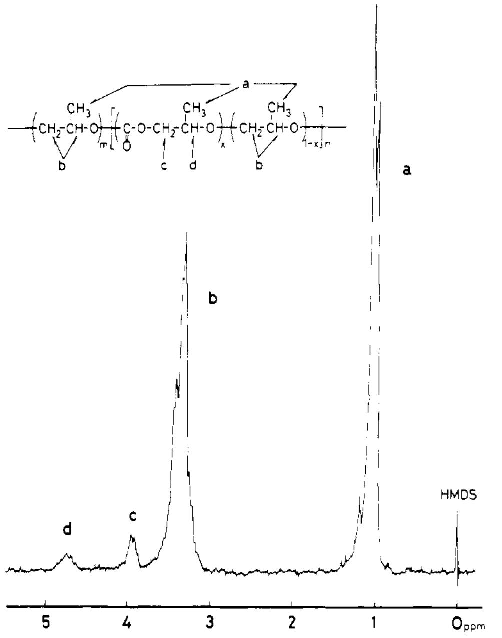


Figure 3. Copolymerization of carbon dioxide and propylene oxide with living poly(propylene oxide). ^1H NMR spectrum of the final product in $CDCl_3$ (run 1 in Table I).

The content of oxycarbonyl units in the blocked chain ($f_{CO_2,block}$) was determined by using the equation

$$f_{CO_2,block} = f_{CO_2,whole} \frac{\bar{M}_{n,whole}}{\bar{M}_{n,whole} - \bar{M}_{n,pre}} \tag{1}$$

where $f_{CO_2,whole}$ is the content of oxycarbonyl units in the final product calculated from the ^1H NMR spectrum (Figure 3) and $\bar{M}_{n,whole}$ and $\bar{M}_{n,pre}$ are the number-average molecular weights of the final product and of the prepolymer used, respectively.

For example, $f_{CO_2,block}$ in run 1 (Table I) was calculated to be 22 mol %, and the blocked chain is not alternating. Similar oxycarbonyl contents were obtained, regardless of whether the reaction was carried out in dichloromethane or dioxane or whether in the dark or with irradiation by visible light (runs 3–5). However, copolymerization under higher pressure of CO_2 (50 $kg \cdot cm^{-2}$, run 2 in Table I) yielded a copolymer with a higher $f_{CO_2,block}$ value (32 mol %).

Although the copolymerization of carbon dioxide and epoxide with an organozinc catalyst system gives alternating copolymer, attempted reactions with 1:1 triethylaluminum–water or a 1:0.5:0.5 triethylaluminum–water–acetylacetone system were reported to give a polymer with a very low oxycarbonyl content, virtually a polyether.[7] However, the addition of triphenylphosphine or 2,2′-bipyridine to triethylaluminum increased the oxycarbonyl content to 22 mol % under a CO_2 pressure of 5 kg·cm^{-2}.[7] Thus, it is interesting to note that the chelating of a porphyrin ligand with aluminum facilitated the attack of the aluminum alkoxide (the living polyether) on carbon dioxide and produced a block copolymer with a similar oxycarbonyl content in its blocked chain under a CO_2 pressure of 8 kg·cm^{-2} (run 1). In this connection, the copolymerization of carbon dioxide (8.1 kg·cm^{-2}) and propylene oxide with (tetraphenylporphinato)aluminum methoxide as catalyst was reported to give a copolymer with an oxycarbonyl content of 40 mol %.[8]

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High Apparent Excluded Volume Exponents: A Comment on the Remarks by Fujita and Norisuye

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Fujita and Norisuye[1] have recently commented on a modified blob model[2] developed in order to explain the exprimental finding of an apparent excluded volume exponent ν_G higher than 0.60 in the crossover region between the Θ regime and the asymptotic excluded volume regime. ν_G is defined as

$$\nu_G(N) = \frac{1}{2}\frac{\partial \ln \langle S^2\rangle}{\partial \ln N} \tag{1}$$

where S is the radius of gyration and N the number of segments.

Their point is that a high value of ν_G implies a similar high value of ν_r, the apparent excluded volume exponent for the mean-square distance $\langle r^2(t)\rangle$ between two segments separated by t units along the chain:

$$\nu_r(t) = \frac{1}{2}\frac{\partial \ln \langle r^2(t)\rangle}{\partial \ln t} \tag{2}$$

This is quite correct since ν_G is a weighted average over ν_r

$$\nu_G = \frac{\int_0^N (1 - t/N)\langle r^2(t)\rangle \nu_r(t)\, \mathrm{d}t}{\int_0^N (1 - t/N)\langle r^2(t)\rangle\, \mathrm{d}t} \tag{3}$$

This seems at first in contradiction with our starting hypothesis:

$$\langle r^2(t)\rangle \propto t^{2\nu(t)} \tag{4}$$

with $0.5 \le \nu(t) \le 0.6$.

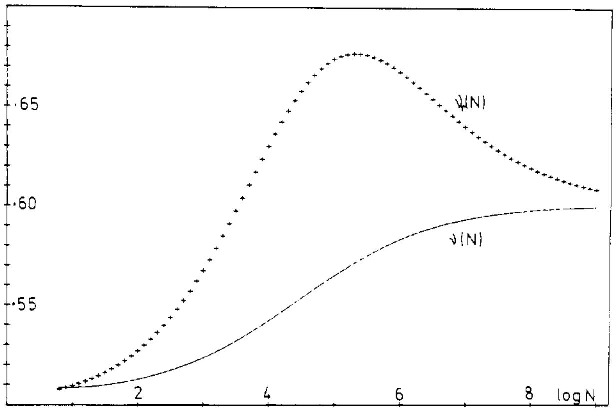

Figure 1. $\nu(N)$ and $\nu_r(N)$ as a function of log N for Ullman's expression of $\nu(t)$ with $v_e = 0.05$.

However, $\nu(t)$ should not be confused with $\nu_r(t)$ since from (4) and (2)

$$\nu_r(t) = \nu(t) + \ln t\, \frac{\partial \nu(t)}{\partial \ln t} \tag{5}$$

$\nu_r(t)$ may therefore exceed the limiting value 0.6 of $\nu(t)$ for many choices of the t dependence of $\nu(t)$.

However, Fujita and Norisuye jump to the conclusion that "...according to the theories available to date for linear flexible chains, $\nu_r(N)$ ($=\partial \log \langle R^2\rangle/\partial \log N$) is a monotonically increasing function of N, where $\langle R^2\rangle$ denotes the mean-square end-to-end distance of the entire chain. We believe that this feature holds for $\nu_r(t)$ as well".

We do not fully agree with these conclusions. What is firmly established from a theoretical point of view is[3] (i) the first-order perturbation expansion relating the swelling ratios α_r and α_s to the excluded volume parameter $z \propto \beta N^{1/2}$, where β is the excluded volume integral,[4] and (ii) the exact excluded volume exponent ν in the asymptotic excluded volume regime $\alpha \propto N^{\nu-1/2}$.[5]

The original Flory formula $\alpha^5 - \alpha^3 = Cz$ gives a value of $\nu = 0.60$, in good agreement with the more exact result 0.5885. But the value of C and the shape of the function $\alpha(z)$ in the crossover region are not as well founded. The original Flory formula with $C = 2.60$ does not fit the perturbation expansion and it has been proposed[6] to retain its $\alpha^5 - \alpha^3$ form and to readjust C to a value 1.276. But it is quite evident on a log α–log z plot that a change in C (which displaces the position of the asymptote) and/or in the shape of $\alpha(z)$ can produce an inflection which is the sufficient condition for ν_r and $\nu_G > \nu$ in the crossover region.

Our choice of $\nu(t)$ certainly overemphasizes this point since the strict choice of $\alpha = 1$ inside a blob of size N_C imposes a point of discontinuity in the log α–log N relation but evidently does not fit the low-α perturbation expansion. We want to show that other choices of $\nu(t)$ which respect this expansion lead also to values of $\nu_r(t) > \nu$.

Ullman has recently proposed[7] an empirical expression of $\nu(t)$ which satisfies the two limiting behaviors (i) and (ii) for α

$$\nu(t) = 0.6 - \frac{0.1}{1 + P(t,N)}$$

$$P(t,N) = v_e f(t,N)/\ln t \tag{6}$$

where $v_e = 5zN^{-1/2}$ is proportional to β and $f(t,N)$ is taken as to fit the low-α perturbation expansion.[3] It therefore depends both on the position of the t segments inside the chain and on the total length N of the chain.

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