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Table I
Rates of Ionization of Ethyl Nitroacetate Catalyzed by Poly(amido amine) B in Aqueous Solutions at 25 °C (Ionic Strength = 0.1 M)

I. Buffer Ratio $[B]/[BH^+] = 1$

$10^4[B]$	2.00	4.00	6.40	10.0
k_{obsd}/s^{-1}	1.39	3.10	4.94	8.25
$k_{calcd}{}^a/s^{-1}$	1.61	3.21	5.14	8.03

II. Buffer Ratio $[B]/[BH^+] = 2$

$10^4[B]$	8.00	16.0	24.0	32.0	48.0
k_{obsd}/s^{-1}	9.60	15.7	22.3	30.3	39.1
$k_{calcd}{}^b/s^{-1}$	9.58	16.2	22.7	29.3	42.5

[a] Calculated from the equation $k_{calcd} = 8.03 \times 10^3[B]$. [b] Calculated from the equation $k_{calcd} = 3.0 + 8.23 \times 10^3[B]$.

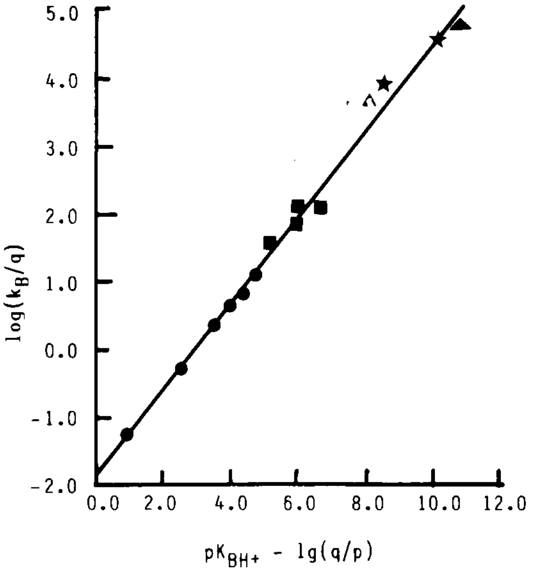

Figure 1. Dependence of the rate of ionization of ethyl nitroacetate upon the strength of the reacting base: (▲) triethylamine; (★) phenoxide ions; (■) pyridines; (●) carboxylate anions;[9] (△) poly(amido amine) B. *p* and *q* are statistical correction terms allowing for the number of dissociable protons (*p*) and the number of equivalent points at which a proton can be attached (*q*) (see also ref 10).

ering the low basicity of BH^+ as compared with that of B: $pK_a(BH_2{}^+) = 4.54$.[2] It may also be pointed out that a smaller contribution by OH^- is detectable only at buffer ratio $[B]/[BH^+] = 2$, as expected from the known value of k_{OH}.[9]

From the above results it may be concluded that the poly(amido amine) studied in the present work acts as catalyst in the ionization reaction of ethyl nitroacetate in a way predictable by the Brøsted equation established for "normal" bases (see Figure 1) (average $k_B = 8.13 \times 10^3$ mol^{-1} dm^3 s^{-1}).

This further confirms that the repeating units of this polymer behave independently and that no significant effects due to macromolecularity are present. To our knowledge, this is first instance in which the catalytic power of a synthetic polymer can be quantitatively related to a thermodynamic quantity of the same polymer, namely, its basicity constant, which, owing to the peculiar nature of poly(amido amines), had been accurately determined.[2]

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Calculation of Spinodals for Quasi-Binary Polymer Systems

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The spinodal is the locus of temperature–concentration pairs for which the Gibbs free energy of mixing has an inflection point.[1] Physically, the spinodal determines limits of metastability of the system. In polymer systems, the free energy function is sensitive to polydispersity.[2] Therefore, a convenient method for locating spinodals, for example, the pulse-induced critical scattering method,[3] could provide a source of information about the systems, including that of the polydispersity of the polymers involved. The free energy function ΔG_{mix} itself should then serve as a means for calibration. For polymers consisting of, say, N components differing in length, the spinodal condition is given by the Gibbs equation[1]

$$\det \{\partial^2 \Delta G_{mix}/\partial\phi_i \partial\phi_j;\ i, j = 1, 2, ..., N\} = 0 \qquad (1)$$

where ϕ's are the concentrations of the components, conveniently expressed as the volume fractions.

Equation 1 becomes more and more difficult to handle as N increases, and for polydisperse polymers with a large number of chain lengths an explicit expression can be derived from it only in special cases.[4] Fortunately, as Irvine and Kennedy have shown in their recent paper,[5] there exists a general method of computing phase diagrams for systems with polymers of arbitrary polydispersity. The method involves free energy functions of the Flory–Huggins[6] type

$$\Delta G_{mix}/\mathcal{N}_1 RT = \sum_{i=0}^{N} \phi_i m_i^{-1} \ln \phi_i + \Gamma \qquad (2)$$

and exploits the expansion of the appropriate conditions (e.g., eq 1 for the spinodal) in terms of moments of the unnormalized molecular weight distribution, defined as[7]

$$M_k \equiv \sum_{i=1}^{N} \phi_i m_i^k \qquad (3)$$

$\mathcal{N}_1$ is the number of lattice "moles" and m_i is the length of the ith chain relative to the size of a solvent molecule (subscript "0"; $m_0 = 1$).

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The term Γ is the semiempirical part of the free energy function that is still in process of development.[8] Existing versions of the Γ term can be expressed as

$$\Gamma = \Gamma(T,\{M_{\mathbf{k}}\}) \qquad (\mathbf{k} = [k_1, k_2, ..., k_n]) \tag{4}$$

where $\{M_{\mathbf{k}}\}$ is denoted as the set of n moments, including

$$M_0 = \sum_{i=1}^{N} \phi_i \equiv \phi = 1 - \phi_0 \tag{5}$$

Equations 3 and 5 reveal the generalizing character of the unnormalized moments that provide information on both concentration (ϕ) and molecular weight distribution.

The decreasing sensitivity of spinodal and critical point loci on moments of increasing order led Gordon et al.[7] to a conclusion, later rigorously proved, that the spinodal depends on only a few moments more than Γ itself. Only another few moments are required to complete the dependence of the critical point position on the molecular weight distribution. Gordon et al. showed that for purposes of calculation a given polydisperse sample could be replaced by a dummy mixture of monodisperse fractions (δ fractions) that shared a desired number of specified moments with the actual polymer but might differ in all others. This trick enabled them to replace very large determinants by much smaller ones in calculating spinodals and critical points. If the Γ function, eq 4, is not expandable in a finite number of moments, the spinodal and critical point positions also depend on an infinite number of moments. In this case, the use of δ-fraction mixtures matching a small number of moments provides an approximate solution.[9]

We will show that for spinodals, in cases when the Γ function is expandable in terms of a finite (usually small) number of moments, calculation of the dummy δ-fraction mixture is not necessary. Therefore, whenever orders of moments in the expansion of the spinodal condition are not equally spaced (see, e.g., ref 10) and the elegant method adopted by Irvine and Kennedy[5] may not be applied, calculation of the exact spinodal locus for systems with a polymer of arbitrary polydispersity remains relatively easy. The method uses the explicit moment expansion of the spinodal condition devised by Irvine and Gordon[11] in their proof of the "truncation" theorem.

The elements of the matrix in eq 1 can be written in the form

$$\partial^2 \Delta G_{\text{mix}}/\partial\phi_i \partial\phi_j = \phi_0^{-1} + \delta_{i,j}(\phi_i m_i^{-1}) + \sum_{r=k_1}^{k_n} \sum_{s=k_1}^{k_n} \frac{\partial^2 \Gamma}{\partial M_r \partial M_s} \frac{\partial M_r}{\partial \phi_i} \frac{\partial M_s}{\partial \phi_j} \tag{6}$$

where $\delta_{i,j}$ is the Kronecker delta. Thus, at the spinodal, a determinant of the matrix

$$\mathbf{S} = \mathbf{I} + \mathbf{V} \tag{7}$$

obtained by rearrangement of (6), where the elements of $\mathbf{V}$ are

$$\{V\}_{i,j} \equiv \sum_r \sum_s C_{r,s} \phi_i m_i^{r+1} m_j^s \tag{8}$$

and

$$C_{r,s} \equiv \frac{\partial^2 \Gamma}{\partial M_r \partial M_s} + \delta_{0r}\delta_{0s}\phi_0^{-1} \tag{9}$$

vanishes. It is useful to remark that the vanishing of det $\{\mathbf{S}\}$ is equivalent to

$$\sum_{i=0}^{N} \text{tr}_i\ \mathbf{V} = 0 \tag{10}$$

where the lth trace, $\text{tr}_l\ \mathbf{V}$, is the sum of the principal minors of order l of det $\{\mathbf{V}\}$[12] and

$$\text{tr}_0\ \mathbf{V} \equiv 1 \tag{11}$$

It is not difficult to verify that all $\text{tr}_p\ \mathbf{V}$ vanish for $p \geq 2n$ (n is defined in eq 4), which justifies the truncation. Moreover, making use of reindexing of the elements of the minors of $\mathbf{V}$, which is consistent with general properties of determinants, Irvine and Gordon[11] showed that eq 1 (or eq 10) can be written as

$$\mathcal{O}(|\mathbf{P}|) = -1 \tag{12}$$

and

$$\mathbf{P} = \mathbf{C}\cdot\mathbf{M} \tag{13}$$

is the $n \times n$ matrix. The elements of the matrix $\mathbf{C}$ are given by (9) while the symmetric matrix $\mathbf{M}$ consists of at most $n(n + 1)/2$ moments (not necessarily all distinct), given as

$$\{M\}_{i,j} \equiv M_{k_i+k_j+1} \tag{14}$$

and $\mathcal{O}(\,)$ stands for the operation of adding to a determinant the sum of all its minors.

The explicit equation (12) allows calculation of spinodals directly from the moments of the molecular weight distribution, without need for substituting mixtures of δ fractions, but for computing critical points, this is still necessary.

Often the model free energy function involves the form (cf. eq 2 and 4)

$$\Gamma = \Gamma_1(T,M_0) + \Gamma_2(\{M_{\mathbf{k}}\}) \tag{15}$$

for example, Γ_1 may have the form proposed for polymer solutions by Orofino and Flory:[13]

$$\Gamma_1 = \phi\phi_0(\beta_0 + \beta_1/T)/(1 - \gamma\phi) \tag{16}$$

where β_0, β_1, and γ are adjustable parameters, and if T can be found explicitly as $T = T(\Gamma_1)$, then spinodal temperatures are available explicitly without the iteration procedures used previously.[5] Thus, let $M_{k_j} = M_0$. Then, each element of the jth row of the matrix $\mathbf{P}$ has an element $C_{j,j}M_{j,q}$ ($q = 1, 2, ..., n$). If we define two new matrices, a matrix $\mathbf{R}$ having all elements of $\mathbf{P}$ except the $C_{j,j}M_{j,q}$ terms and a matrix $\mathbf{Q}$ differing from $\mathbf{P}$ only by having the jth row composed of $M_{j,q}$'s, then the condition (12) can be rewritten as

$$\mathcal{O}(|\mathbf{R}|) + C_{j,j}\mathcal{O}_j(|\mathbf{Q}|) + 1 = 0 \tag{17}$$

and finally, for Γ_1 defined by (16), the spinodal temperature will be given by

$$T_{\text{sp}} = \beta_1 \left[\frac{(1 - \gamma M_0)^3}{2(1 - \gamma)} \left\{ \frac{1 + \mathcal{O}(|\mathbf{R}|)}{\mathcal{O}_j(|\mathbf{Q}|)} + (1 - M_0)^{-1} + \partial^2\Gamma_2/\partial M_0^{\,2} \right\} - \beta_0 \right]^{-1} \tag{18}$$

Here $\mathcal{O}_j(\,)$ stands for a new operator that adds to a determinant the sum of all those minors which contain at least one element of the jth row.

From the practical point of view, one must exclude limiting cases of the form $\partial\Gamma/\partial M_j \equiv 0$, $j \in \mathbf{k}$; this degenerate case of eq 4 (which means that Γ does not actually depend on M_j) invalidates eq 12, unless n is adjusted to $n - 1$. The computer program requires the proper specification of n (eq 4).

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

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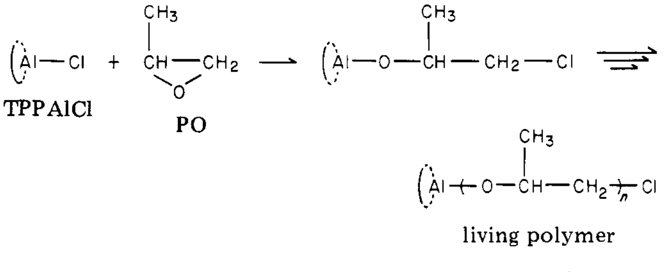
Chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization.[1] We have studied in detail the alternating copolymerization of carbon dioxide and epoxide, mainly by using a diethylzinc-based system, to give polycarbonates of high molecular weight[2] but very broad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



TPPAlCl PO

living polymer

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 ^1H 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 ^1H 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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