The Effect of Limited Monomer Solubility in Heterogeneous Step-Growth Polymerization

YING-HUNG SO

The Dow Chemical Company, Advanced Electronic Materials Laboratory, 1712 Building, Midland, Michigan 48674

Received January 12, 2001

ABSTRACT

Limited monomer solubility imposes very intriguing features on poly(*p*-phenylenebenzobisoxazole) polymerization. Only one type of functional group is detected at oligomer chain ends, and a high-molecular-weight polymer is obtained even when an excess of the monomer with low solubility is used. These remarkable phenomena are interpreted as an unprecedented "spoon-feeding-of-monomer" mechanism. A novel apparatus for staged polymerization is described that was triggered by the uniqueness of the heterogeneous step-growth polymerization. Hyperbranched polyesters and a polyurethane/polyethylene blend, which represent two phases in the polymerization process, are also discussed.

Introduction

In A–A plus B–B step-growth polymerization, a linear chain is obtained by the stepwise intermolecular condensation or addition of the reactive groups in bifunctional monomers. The molecular weight distribution (MWD) of
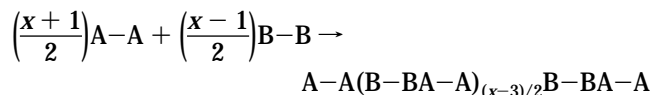
$$A\text{--}A \ + \ B\text{--}B \ \longrightarrow \ \left[\!\!\begin{array}{c}\text{A--AB--B}\end{array}\!\!\right]_n$$

step-growth systems was analyzed by Flory with the assumption that all functional groups can be considered as being equally reactive.[1] Three types of molecules with respect to the end-group functionality may be formed in the polymeric mixture.
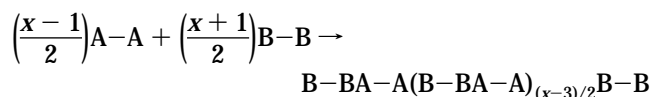
If *x*, the total number of reactant molecules combined in the polymer molecule, is an even integer,

$$\left(\frac{x}{2}\right)A\text{--}A + \left(\frac{x}{2}\right)B\text{--}B \rightarrow A\text{--}A(B\text{--}BA\text{--}A)_{(x-2)/2}B\text{--}B$$

If *x* is odd, either

$$\left(\frac{x+1}{2}\right)A\text{--}A + \left(\frac{x-1}{2}\right)B\text{--}B \rightarrow$$
$$A\text{--}A(B\text{--}BA\text{--}A)_{(x-3)/2}B\text{--}BA\text{--}A$$

or

$$\left(\frac{x-1}{2}\right)A\text{--}A + \left(\frac{x+1}{2}\right)B\text{--}B \rightarrow$$
$$B\text{--}BA\text{--}A(B\text{--}BA\text{--}A)_{(x-3)/2}B\text{--}B$$

Ying-Hung So was born in Hong Kong in 1948. He received his B.S. degree in chemistry from Chung Chi College, The Chinese University of Hong Kong. He began his graduate studies in organic chemistry at Colorado State University with Professor Larry Miller. In 1981, he joined The Dow Chemical Company and is currently a technical leader. His research interests include photosensitive polymers, low-*k* polymers, polymerization mechanism, polymer photodegradation and stabilization, and monomer synthesis. Ying-Hung So is also an honorary associate professor at The University of Hong Kong, where he teaches industrial polymer chemistry and industrial organic chemistry.
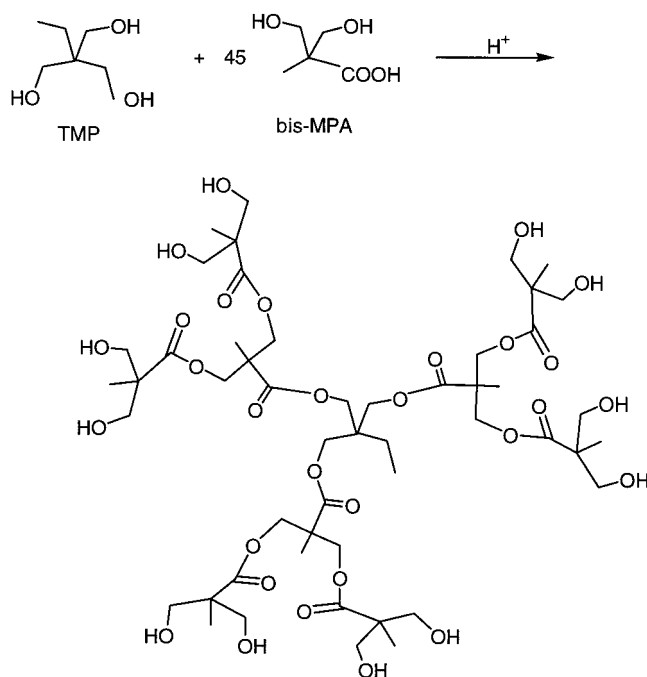

FIGURE 1. A two-dimensional theoretical representation of a hyperbranched polyester synthesized from bis-MPA and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) as the core.

The influence of inherent and induced functional group unequal reactivity on polymerization kinetics and MWD has also been studied.[2,3] Examples of unequal reactivity of functional groups include 2,4-tolylene diisocyanate in polyurethane synthesis,[4] ethylene glycol with dimethyl terephthalate as the other monomer in poly(ethylene terephthalate) production,[5] and sodium *p*-fluorothiophenoxide as a polyphenylene sulfide (PPS) monomer.[6] In all the above cases, the monomers are totally miscible with each other and completely soluble in the reaction medium.

There are a number of industrially important polymerization examples in which the solubility of one of the monomers is limited. For example, the solubility of terephthalic acid (TA) in ethylene glycol for poly(ethylene terephthalate) preparation is very low.[7] In PPS synthesis from *p*-dichlorobenzene and sodium sulfide in *N*-methylpyrrolidinone (NMP), sodium sulfide has limited solubility in the reaction solvent.[8] When hyperbranched polyesters were made from 2,2-bis(methylol)propionic acid (bis-MPA) and different polyols, the miscibility of the polyol and bis-MPA played an important role in the reaction kinetics and polymerization product.[10] A system with a low-melting polyol and good solubility of bis-MPA in the polyol melt exhibited the highest rate of reaction. However, a reaction mixture consisting of a polyol and partly soluble bis-MPA, in which solid bis-MPA gradually dissolved in the melt as the reaction proceeded, was a better choice for achieving a high degree of branching. A phase-separated system allowed complete reaction of all the hydroxyl groups on the core molecule (the polyol) to generate a hyperbranched polyester with a high degree of branching. Figure 1 illustrates a two-dimensional

theoretical representation of a hyperbranched polyester synthesized from bis-MPA and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) as the core.

Preparation of a polyethylene/polyurethane blend polymer via in situ polymerization of diols and diisocyanate monomers dispersed in a molten polyethylene matrix was recently reported.[11] High solubility of isocyanate monomers and low solubility of alcohols in molten polyethylene induced an unbalanced stoichiometry, which limited the molecular weight of the polyurethane. The difference in viscosity between polyurethane and polyethylene had a controlling influence on the blend morphology developed. Mathematical modeling of a heterogeneous step-growth polymerization reaction in which a monomer has limited solubility has been reported, and the influence of various operating parameters on the molecular weight and MWD has also been discussed.[12,13]

This Account reviews a detailed study of a heterogeneous polymerization reaction, that is, the preparation of poly([benzo(1,2-d:5,4-d′)bisoxazole-2,6-diyl]-1,4-phenylene) (PBO) with 1,3-diamino-4,6-dihydroxybenzene dihydrochloride (DADHB·2HCl) and TA as starting materials in polyphosphoric acid (PPA).
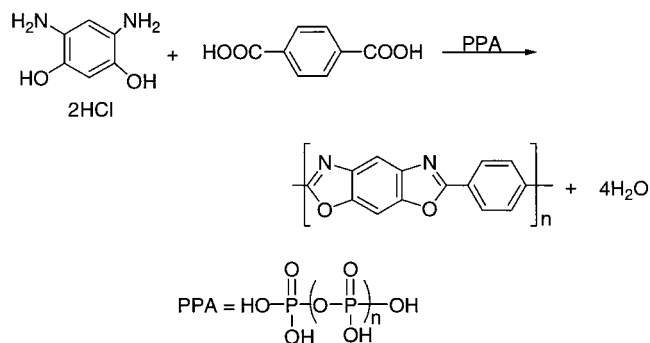

The remarkable facts that only one type of functional group, *o*-aminophenol, is detected at oligomer chain-ends and that high-molecular-weight PBO is obtained even when an excess of TA is used are attributed to the very low solubility of TA in PPA and the heterogeneous nature of the reaction. The unusual oligomer structure triggered an unprecedented method to control PBO molecular weight. Heterogeneous step-growth polymerization is a little-explored field.[14] A review of the mechanism of a heterogeneous step-growth polymerization reaction would be of great value for researchers in academia and industry alike. Some of its unique features may motivate researchers to design new chemistry and a novel polymerization apparatus to meet their needs.

The focus of this Account is on the consequence of limited monomer solubility in step-growth polymerization. Polycondensation of glycols and dicarboxylic acids in acidic water-in-oil emulsions, microemulsions, or solid-in-liquid dispersions to form polyesters is not within the scope of this discussion.[15]

Solubility of TA in PPA for PBO Polymerization

PBO is a rigid-rod-like polymer recently commercialized by Toyobo Company, Japan.[16] PBO fiber is superior to *p*-aramid fibers in tensile strength and modulus. It also has outstanding flame resistance and thermal stability among organic fibers. Mechanistic studies on PBO polymerization in PPA have been pursued at SRI International, The Dow Chemical Company, and other institutions.[17−20]

PPA is a complex mixture of orthophosphoric acid, pyrophosphoric acid, and higher condensed phosphoric acid oligomers that can be represented by the general formulation $H_{n+2}P_nO_{3n+1}$, where $n = 1, 2, 3, ...$[21] The average chain length depends on the ratio of water and P_2O_5. In PPA, dissolved TA exists as the diacid, as α-(4-carboxybenzoyl)-ω-hydroxypoly(oxyphosphinico) (a mono-acid-monoanhydride), and as α,α′-[1,4-phenylenebis(carbonyl)]bis(ω-hydroxypoly(oxyphosphinico) (a dianhydride). Studies by ^{1}H and ^{31}P NMR spectroscopy have demonstrated that the three TA species and PPA are in dynamic equilibrium. High P_2O_5 content in PPA favors the formation of the anhydride.
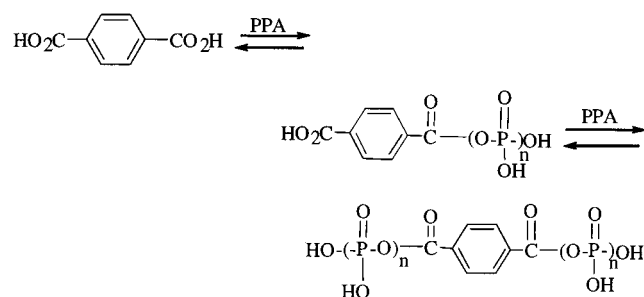
TA has very limited solubility in PPA. The sum of the three dissolved species is 0.0006 g in 1 g of PPA with 86 wt % P_2O_5 at 140 °C. At 100 °C, the solubility is 0.0002 g per g of PPA. In PBO synthesis with 14 wt % of polymer in PPA, the initial concentration of TA is 0.124 g per g of PPA.[22,23] Most TA exists in the solid phase until it is close to a complete conversion. As dissolved TA is converted to benzoxazole in the course of the reaction, solid TA continuously dissolves to maintain its solubility level in PPA. TA with average particle diameter of less than 10 μm has to be used to make high-molecular-weight PBO.[17,24] The large surface area of micronized TA enhances the dissolution rate of the solid particles and ensures the complete conversion of the monomer for the polymerization reaction.

Unusual Structure of PBO Oligomer

Several PBO oligomer samples were isolated during the course of a polymerization reaction, and some distinctive findings were made. At a given time, conversion of DADHB was always higher than that of the other monomer, TA. A significant amount of phosphorus was found in the oligomer even after repeated water washings. The amount of residual phosphorus decreased as the conversion of reactants increased, as is illustrated in Table 1.
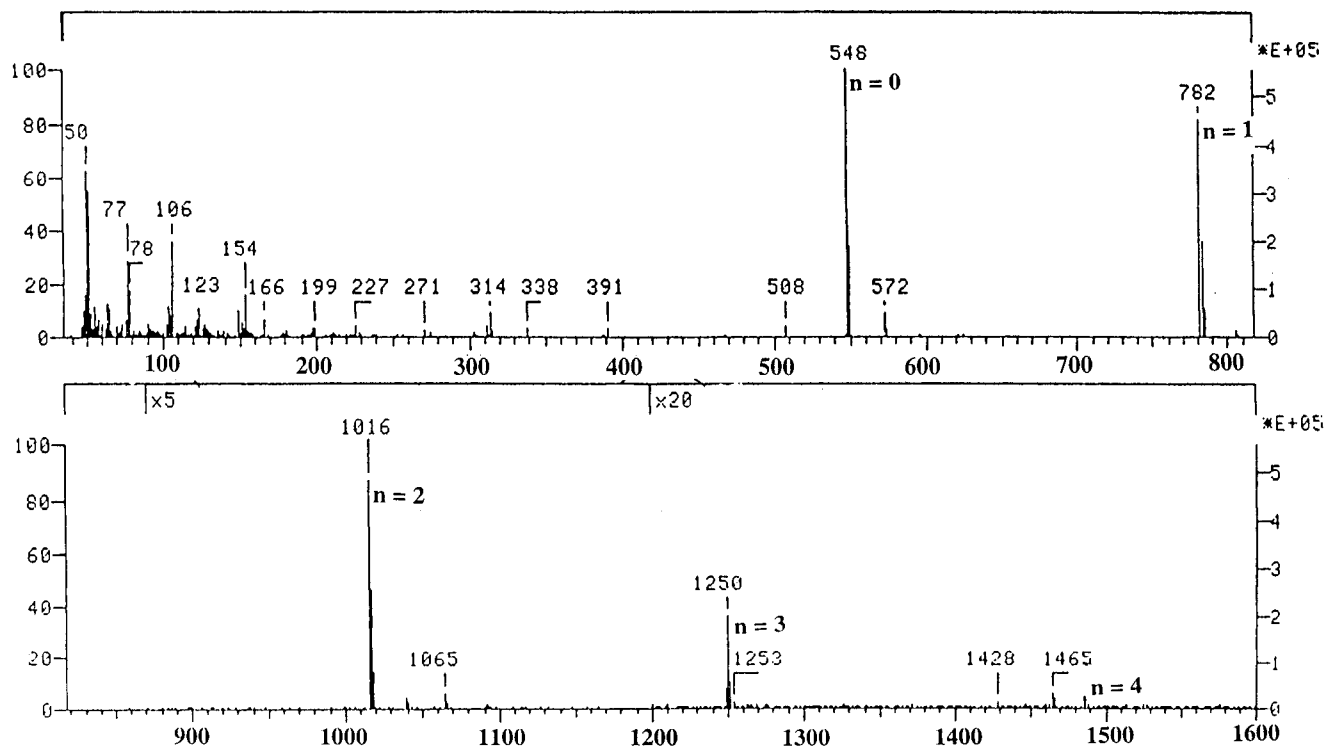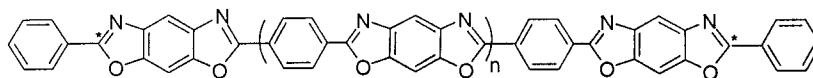
FIGURE 2. MS of the product from *isolated* PBO oligomer and benzoic-*carboxy-¹³C* acid. Only benzoic-*carboxy-¹³C* acid end-capped PBO compounds with up to five TA plus six DADHB were detected.

Table 1. Conversion of Monomers and Residual Phosphorus in Oligomer during PBO Polymerization

reaction time (h)	DADHB conversion	TA conversion	phosphorus in oligomer (%)
5.0	0.67	0.50	6.4
7.1	0.74	0.61	5.8
8.7	0.82	0.66	3.4
10	0.90	0.79	3.0
14	~1	0.93	1.2

IR and ¹³C NMR spectra of the PBO oligomer did not show carboxylic acid. A PBO oligomer structure with both chain-ends capped with one type of functional group was proposed. The fact that the ratio of DADHB conversion to TA conversion decreases as the polymerization progresses is also consistent with the suggested structure. The remarkable structure of the PBO oligomer was further supported by the MS of its condensation product with benzoic-*carboxy-¹³C* acid. The only products detected by MS were benzoic-*carboxy-¹³C* acid end-capped PBO compounds of up to five TA molecules plus six DADHB molecules, as shown in Figure 2. We are the first to fully characterize and report this unique oligomer structure,
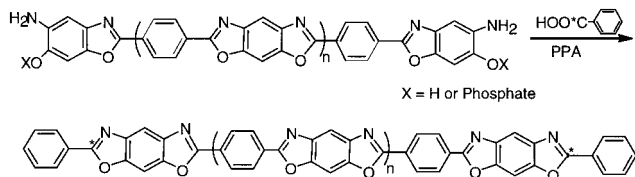
although the predominance of one type of end-group has been suggested for a heterogeneous step-growth polymerization.[12]

The average number of repeating units in the PBO oligomer can be determined by chain-end functional group analysis.[25] Chain-end DADHB functional groups were converted to fluorobenzoxazoles.
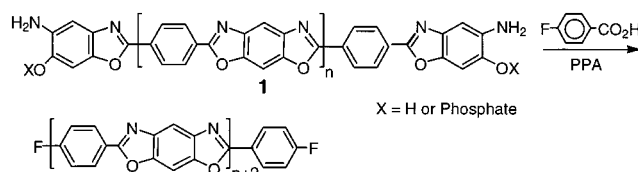
The average number of repeating units was measured by the amount of fluorine incorporated in the polymer. This approach is good for PBO with $\bar{M}_n$ of less than 12 000 g/mol. For high-molecular-weight polymers, degradation of chain-end functional groups or impurities in the monomers can cause significant deviation in $\bar{M}_n$ determination.

A Remarkable Polymerization Mechanism

The unusual structure of the PBO oligomer and extremely low solubility of TA in PPA led to an unprecedented polymerization mechanism, as is shown in Figure 3. TA, with the carbonyl group activated through anhydride formation, reacts with DADHB to form the dimer, 4-[2-
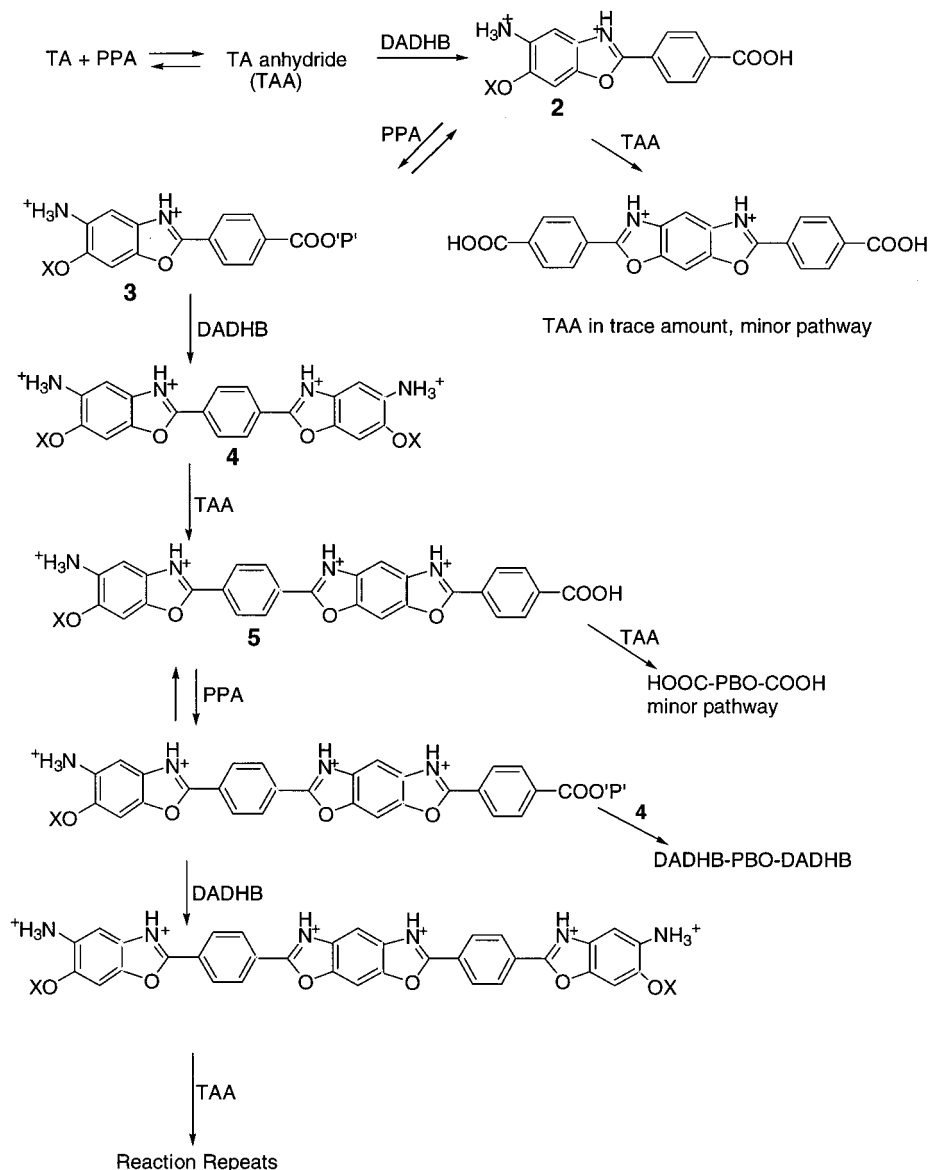
FIGURE 3. Proposed PBO polymerization mechanism, in which one of the monomers has limited solubility in the reaction medium.

(5-amino-6-benzoxazolol)]benzoic acid (**2**). The chance of the *o*-aminophenol end of **2** finding a TA anhydride (TAA) to react with is very low due to the extremely low concentration of TAA in PPA. The carboxylic acid end of **2** can readily react with the solvent, PPA, to form the anhydride, **3**, which then reacts with DADHB to generate the trimer, 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol) (**4**).

Compound **4** must encounter a TAA to produce the tetramer, **5**. Compound **5** has the same fate as **2**. The probability that **5** will form an anhydride with PPA and then react with DADHB or an oligomer end-capped with DADHB is much higher than its probability of encountering a TAA. The proposed mechanism explains why only oligomers end-capped with DADHB are detected. This reaction pattern continues until the concentration of the unreacted DADHB functional group is comparable to that of soluble carboxylic acid anhydride. IR and NMR spectra of the isolated oligomer did not show any esters or amides, or their hydrolysis products. The result is consistent with

Hodd's suggestion that the benzoxazole ring-closure reaction is fast in the presence of an acid catalyst.[26]

In linear polymerization A–A plus B–B, one must precisely adjust the stoichiometric balance of the bifunctional monomers. The number-average degree of polymerization $\bar{X}_n$ with stoichiometric unbalanced r at complete conversion is

$$\bar{X}_n = \frac{(1 + r)}{(1 - r)}$$

With 5 mol % excess of one monomer, the maximum $\bar{X}_n$ is about 20. Surprisingly, high-molecular-weight PBO was obtained even when TA was in excess.[27,28] This unusual phenomenon is explained by the extremely low solubility of TA in the reaction medium, PPA. Only TA species that dissolve in PPA participate in PBO polymerization at a given time. As polymerization progresses, dissolved TA is consumed and solid TA gradually dissolves to maintain the TA solubility level at the reaction temperature. TA is

"spoon-fed" to the reaction medium until TA content is at or below its solubility limit in PPA. Excess solid TA does not participate in the reaction, and, therefore, high-molecular-weight PBO is obtained at high DADHB functional group conversion. On the other hand, only low-molecular-weight PBO was obtained when excess DADHB was used. As with conventional A−A plus B−B step-growth polymerization with stoichiometric imbalance, the $\bar{X}_n$ is limited by the conversion of the DADHB functional group at complete TA conversion.

Polydispersity Index in a Heterogeneous Step-Growth Polymerization

Ravindranath discussed the polydispersity index (PDI) of a heterogeneous step-growth polymerization, where the solubility of A−A is limited, as a function of unreacted B functional groups.[12] For a case in which the weight ratio of dissolved A−A to reaction mixture (α) was 0.01, calculated PDI was around 2 at above 60% conversion of B functional groups.

Two PBO oligomer samples were isolated and then end-capped with *p*-fluorobenzoic acid. The fluorine contents of the products suggested an *n* of 33.5 and 50 in structure **1**, which corresponded to an $\bar{M}_n$ of 8×10^3 and 12×10^3 g/mol, respectively. Since analysis of the polymer solution samples showed essentially no residual DADHB monomer, conversion of DADHB functional groups was 97% and 98% based on the *n* values. Light-scattering results of the two samples showed an $\bar{M}_n$ of 16×10^3 and 22×10^3 g/mol, with 10% experimental error.[29] Molecular weight determination data indicated that PBO, a step-growth polymer in which one of the monomers has very low solubility in the medium, has a PDI of about 2. The experimental results are consistent with Ravindranath's calculation.

A Novel Apparatus for Molecular Weight Control

Molecular weight control in linear polymerization is crucial in achieving the balance of mechanical properties and processibility. The two most common methods for molecular weight control are the adjustment of the concentration of the two monomers so that they are slightly nonstoichiometric and the addition of a small amount of a monofunctional monomer. However, accurate transfer of the monomers into a reactor can be challenging, especially when appropriate solvents cannot be used to rinse the weigh containers.

Because of the unique structure of PBO, the *isolated* PBO oligomer molecular weight can increase again when PBO is redissolved in PPA, followed by the addition of TA. This phenomenon triggered an unprecedented plant-scale design for linear polymer molecular weight control.[22,30] TA is short-loaded at the beginning of the polymerization reaction to generate an oligomer mixture end-capped with DADHB. The reaction mixture is then pumped through a twin-screw extruder. A slurry of TA in PPA is added to the extruder through a syringe pump, as is shown in Figure
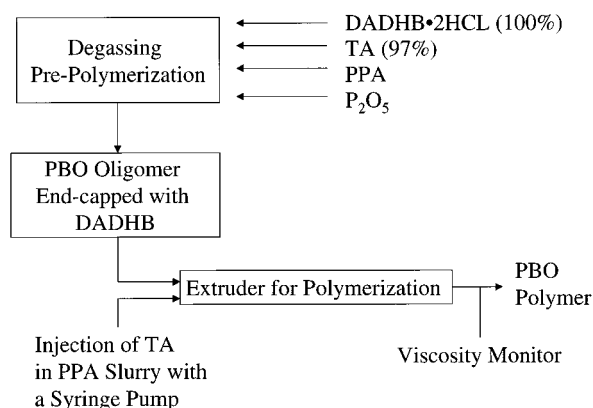

FIGURE 4. Diagram for staged PBO polymerization with a novel design for molecular weight control.

4. The molecular weight of PBO, which is monitored by the viscosity of the polymer solution exiting the extruder, is adjusted by controlling the amount of TA added to the oligomer mixture. This novel method works very well for producing the PBO polymer with controlled molecular weight, which is critical in fiber spinning.

Concluding Remarks

This Account reviews the unique features of a heterogeneous step-growth polymerization reaction in which one of the monomers has limited solubility. An unprecedented polymerization mechanism is proposed that accounts for the fact that only one type of functional group is detected at the oligomer chain-ends and that a high-molecular-weight polymer is obtained even when one of the monomers is in excess. Limited monomer solubility is practically equivalent to the continuous addition of a monomer during a polymerization reaction. A good understanding of this relatively unexplored field will enable us to take advantage of its unique characteristics to design chemistry and equipment to achieve our objectives. The polymerization apparatus described herein for controlling polymer molecular weight, the remarkable high degree of branching obtained in hyperbranched polyesters that makes use of a phase-separation phenomenon, and the system for governing blend morphology development in a polyurethane/PE blend are some examples. A different dicarboxylic acid can be added to the *isolated* PBO oligomer or through the syringe pump in the apparatus to make segmented block copolymers. More examples that take advantage of the uniqueness of heterogeneous step-growth polymerization are expected to emerge in the future.

References

(1) Flory, P. J. Molecular Size Distribution in Linear Condensation Polymers. *J. Am. Chem. Soc.* **1936**, *58*, 1877−1885.
(2) (a) Gandhi, K. S.; Babu, S. V. Kinetics of Step Polymerization with Unequal Reactivities. *AIChE J.* **1979**, *25*, 266−272. (b) Gandhi, K. S.; Babu, S. V. Step Polymerization with Unequal Reactivities of Functional Groups. *Macromolecules* **1980**, *13*, 791−798.

(3) Ozizmir, E.; Odian, G. Kinetics of Step Polymerization with Reactants of Unequal Functional Group Reactivity. *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 1089−1097.

(4) (a) Brock, F. H. Reactivity of Aryl Isocyanates. *J. Org. Chem.* **1959**, *24*, 1802−1804. (b) Brock, F. H. Kinetics of the 2,4-Tolylene Diisocyanate−Alcohol Reaction. *J. Phys. Chem.* **1961**, *65*, 1638−1639.

(5) (a) Yamanis, J.; Adelman, M. Significance of Oligomerization Reactions in the Transesterification of Dimethyl Terephthalate with Ethylene Glycol. *J. Polym. Sci.: Polym. Chem. Ed.* **1976**, *14*, 1945−1959. (b) Yamanis, J.; Adelman, M. Two Models for the Kinetics of the Transesterification of Dimethyl Terephthalate with Ethylene Glycol. *J. Polym. Sci.: Polym. Chem. Ed.* **1976**, *14*, 1961−1973.

(6) Lenz, R. W.; Handlovits, C. E.; Smith, H. A. Phenylene Sulfide Polymers III. The Synthesis of Linear Polyphenylene Sulfide. *J. Polym. Sci.* **1962**, *58*, 351−367.

(7) (a) Goodman, I. Direct Esterification Process. In *Encyclopedia of Polymer Science and Technology*, 2nd ed.; Mark, H. F., Kroschmitz, J. I., Eds.; Wiley-Interscience: New York, 1988; Vol. 12, pp 45−46. (b) Poly(ethylene terephthalate). Japanese Patent 55,112,232, August 29, 1980, assigned to Japan Ester Co., Japan.

(8) (a) Edmonds, J. T., Jr.; Hill, H. W., Jr. (Phillips Petroleum Co.). Production of Polymers from Aromatic Compounds. U.S. Patent 3,354,129, November, 1967; *Chem. Abstr.* **1967**, *68*, 13,598c. (b) Rajan, C. R.; Ponrathnam, S.; Nadkarni, V. M. Poly(phenylene Sulfide): Polymerization Kinetics and Characterization. *J. Appl. Polym. Sci.* **1986**, *32*, 4479−4490. (c) Lopez, L. C.; Wilkes, G. L. Poly(*p*-Phenylene Sulfide)—An Overview of an Important Engineering Thermoplastic. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29* (1), 83−151. (d) Geibel, J. F.; Campbell, R. W. Poly(phenylene Sulfide)s. In *Comprehensive Polymer Science, Vol. 5, Step Polymerization*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989; pp 543−560. Fahey and co-workers reported that NMP reacts with hydrated Na₂S at elevated temperatures to produce an equimolar mixture of sodium 4-(*N*-methylamino)butanoate with sodium hydrosulfide, which is soluble in the reaction medium.[9] They claimed a homogeneous polymerization reaction dominated by the ionic S$_N$Ar mechanism for the Phillips Petroleum PPS synthesis procedure. However, in most of the examples by Edmonds and Hill, water of hydration in sodium sulfide nonahydrate was removed at 160 °C with nitrogen flush or azeotropic distillation with toluene prior to polymerization. Rajan and co-workers used sodium sulfide, which has limited solubility in NMP, in their study on PPS polymerization kinetics and characterization.

(9) (a) Fahey, D. R.; Ash, C. E. Mechanism of Poly(*p*-phenylene Sulfide) Growth from *p*-Dichlorobenzene and Sodium Sulfide. *Macromolecules* **1991**, *24*, 4242−4249. (b) Fahey, D. R.; Hensley, H. D.; Ash, C. E.; Senn, D. R. Poly(*p*-phenylene sulfide) Synthesis: A Step-Growth Polymerization with Unequal Step Reactivity. *Macromolecules* **1997**, *30*, 387−398.

(10) (a) Malmstrom, E.; Johansson, M.; Hult, A. Hyperbranched Aliphatic Polyesters. *Macromolecules* **1995**, *28*, 1698−1703. (b) Malmstrom, E.; Hult, A. Kinetics of Formation of Hyperbranched Polyesters Based on 2,2-Bis(methylol)propionic Acid. *Macromolecules* **1996**, *29*, 1222−1228.

(11) (a) Cassagnau, P.; Nietsch, T.; Bert, M.; Michel, A. Reactive Blending by in Situ Polymerization of the Dispersed Phase. *Polymer* **1998**, *40*, 131−138. (b) Cassagnau, P.; Nietsch, T.; Bert, M.; Michel, A. Bulk and Dispersed Phase Polymerization of Urethane in Twin Screw Extruders. *Int. Polym. Processing* **1999**, *14*, 144−151.

(12) Ravindranath, K. Analysis of Heterogeneous Step Polymerization with Unequal Reactivities. *Polymer* **1990**, *31*, 2178−2184.

(13) Tung, L. H. A Stepwise Scheme for the Calculation of Molecular Weight Distribution in Condensation Polymers. II. Scheme for Bimolecular Condensation Polymers. *J. Appl. Polym. Sci.* **1993**, *50*, 381−391.

(14) (a) Gupta, S. K.; Kumar, A. Simulation of Step Growth Polymerizations. *Chem. Eng. Commun.* **1983**, *20*, 1−52. (b) *Comprehensive Polymer Science, Vol. 5, Step Polymerization*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989. (c) *Step-Growth Polymers for High-Performance Materials; New Synthetic Methods*; Hedrich, J. L., Labadie, J. W., Eds.; ACS Symposium Series 624; American Chemical Society: Washington, DC, 1996.

(15) Jong, L.; Saam, J. C. Polycondensation of Carboxylic Acids and Carbinols in Heterogeneous Media. In *Step-Growth Polymers for High-Performance Materials, New Synthetic Methods*; Hedrich, J. L., Labadie, J. W., Eds.; ACS Symposium Series 624; American Chemical Society: Washington, DC, 1996; pp 332−349.

(16) In October 1998, Toyobo Company, Japan, announced the commercialization of PBO fiber with Zylon as trademark.

(17) Wolfe, J. F. Polybenzothiazoles and Polybenzoxazoles. In *Encyclopedia of Polymer Science and Technology*, 2nd ed.; Mark, H. F., Kroschmitz, J. I., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, pp 601−635.

(18) (a) So, Y. H.; Heeschen, J. P.; Murlick, C. L. A Mechanistic Study of Polybenzoxazole Formation with Model Compounds. *Macromolecules* **1995**, *28*, 7289−7290. (b) So, Y. H.; Heeschen, J. P. Mechanism of Polyphosphoric Acid and Phosphorus Pentoxide-Methanesulfonic Acid as Synthetic Reagents for Benzoxazole Formation. *J. Org. Chem.* **1997**, *62*, 3552−3561. (c) So, Y. H.; Heeschen, J. P.; Bell, B.; Briggs, M.; Bonk, P.; DeCaire, R. Study of the Mechanism for Poly(*p*-phenylene)benzoxazole Polymerization—A Remarkable Reaction Pathway to Make Rigid-Rod Polymers. *Macromolecules* **1998**, *31*, 5229−5239.

(19) (a) Cotts, D. B.; Berry, G. C. Polmerization Kinetics of Rigid Rodlike Molecules: Polycondensation of Poly([benzo(1,2-d:5,4′)bisoxazole-2,6-diyl]-1,4-phenylene). *Macromolecules* **1981**, *14*, 930−934. (b) Spencer, C. P.; Berry, G. C. Polymerization Kinetics of Rigid-Rod-Like Molecules: 2. Polymerization of Poly(1,4-phenylene-2,6-benzobisthiazole) in the Nematic State. *Polymer* **1992**, *33*, 1909−1913.

(20) *The Materials Science and Engineering of Rigid-Rod Polymers*; Adams, W. W., Eby, R. K., McLemore, D. E., Eds.; Symposium Proceedings; Materials Research Society: Pittsburgh, PA, 1989; Vol. 134.

(21) Popp, F. D.; McEwen, W. E. Polyphosphoric Acid as a Reagent in Organic Chemistry. *Chem. Rev.* **1958**, *58*, 321−401.

(22) Gregory, T.; Hurtig, C. W.; Ledbetter, H. D.; Quackenbush, K. J.; Rosenberg, S.; So, Y.-H. (The Dow Chemical Co.). Staged Polymerization of Polybenzazole Polymers. U.S. Patent 5,194,568, 1993.

(23) Production of high-molecular-weight PBO requires a high polymer concentration, which is accompanied by an anisotropic phase. Jim Wolfe and workers at the Wright-Patterson Air Force Base proposed that the dissolved TA molecules would link the aligned rigid-rod-like oligomers, thus allowing for rapid molecular weight build-up.[17]

(24) So, Y.-H. Poly(terephthalic acid anhydride) (as a Latent Monomer). In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 9, pp 6875−6878.

(25) So, Y.-H.; Suter, U. W.; Romick, J. Determination of Poly(*p*-phenylene)benzoxazole Number Average Molecular Weight. *Polym. Preprints, Am. Chem. Soc. Div. Polym. Chem.* **1999**, *40* (2), 628−629.

(26) (a) Hodd, K. A. Studies of Heterocyclic Polymers. Part IV. Weight-change studies of the Catalyzed and Uncatalyzed Formation of Poly(benzoxazoles) by the Cyclodehydration of Some Poly(*o*-hydroxyanides). *Therm. Anal.*; ICTA: Budapest, 1974; Vol. 2, pp 91−103. (b) Ghaffari, F.; Hodd, K. A. Studies in Heterocyclic Polymers. Part VI. A Weight-Loss Study of the Formation of a Polybenzoxazole. *Thermochim. Acta* **1980**, *41*, 213−224.

(27) Tsai, T. T.; Arnold, F. E.; Hwang, W. F. Synthesis and Properties of High Strength High Modulus ABA Block Copolymers. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2839−2848.

(28) Similar phenomena were reported in PPS synthesis from sodium sulfide and *p*-dichlorobenzene with NMP as solvent. A perfect 1:1 stoichiometric monomer ratio is not required to make high-molecular-weight PPS, and polymer molecular weight is higher than expected at incomplete conversion of monomers. However, PPS polymerization chemistry is still under dispute. Whether PPS polymerization proceeds by an S$_N$Ar process, by a single-electron-transfer process with radical cations as reactive intermediates, by an S$_{RN}$1 process, or by a combination of the above three processes has not been established. As a result, it is difficult to relate the observations made in PPS polymerization to the discussion on heterogeneous step-growth polymerization in this Account.

(29) Roitman, D. B.; Wessling, R. A.; McAlister, J. Characterization of Poly(*p*-phenylene-cis-benzobisoxazole) in Methanesulfonic Acid. *Macromolecules* **1993**, *26*, 5174−5184.

(30) So, Y.-H. Rigid-Rod Polymers with Enhanced Lateral Interactions. *Prog. Polym. Sci.* **2000**, *25*, 137−157.

AR0100069