Novel Production Methods for Isobutylene Based Polymers

Synopsis

Isobutylene forms the basis for 3 commercially important polymers: polybutenes, polyisobutylene (PIB), and butyl rubber (IIR). The markets for these products are well established and growing, especially in developing Asia.[1] Industrial methods for the production of these materials exist and have been in practice for many years but are not ideal as they are costly and polluting.[2] Our research group has developed a new method for the preparation of high molecular weight grades of PIB and butyl rubber that offers both cost and environmental benefits.[3]

Market Overview

Polyisobutylene (Figure 1) is a well-defined homopolymer of isobutylene. Depending on

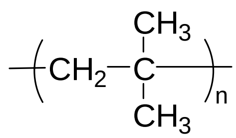

Figure 1

the number average molecular weight ($\overline{M}_n$) physical properties can range from liquids to semiliquids and solids. End uses include lubricants, sealants, and adhesives. A process referred to as *chain transfer* limits ultimate polymer molecular weights and can be suppressed by reducing the polymerization temperature.[4] Since $\overline{M}_n$ is inversely proportional to the polymerization temperature (Figure 2) the manufacture of high $\overline{M}_n$ PIBs is costly. Traditional

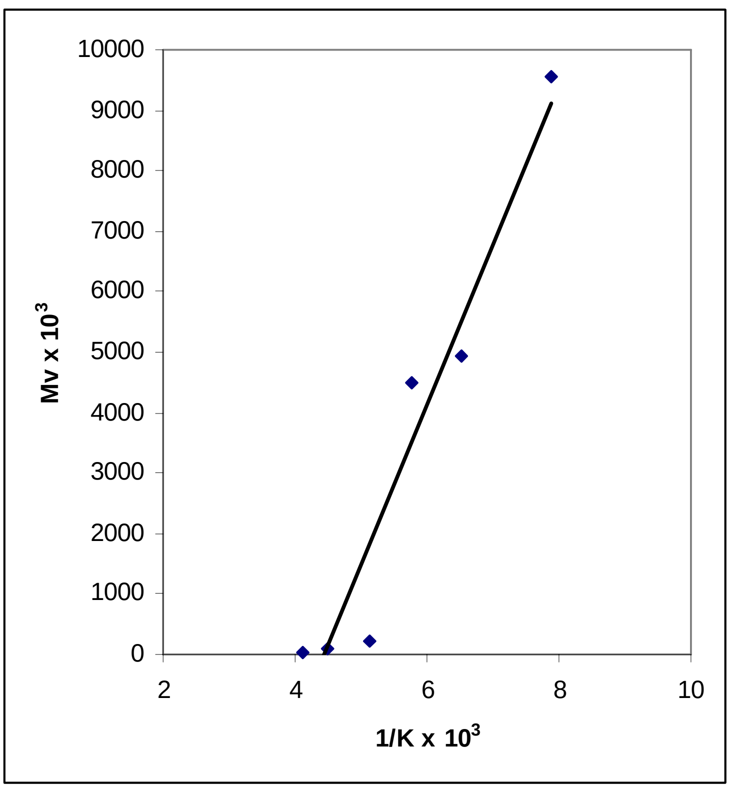

Figure 2. Viscosity Average Molecular Weight PIB versus the inverse of temperature ($AlCl_3/CH_3Cl$).[5]

methods[2a] for the preparation of high molecular weight PIBs (> 10^5 g mol^{-1}) require polymerization temperatures ≤ -100 °C in order to reduce chain transfer to an acceptable level. In some cases[2b-f] (processes using $AlCl_3$) toxic solvents (*e.g.* methyl chloride) are required for polymerization; strict regulations prohibit the building of new or expansion of existing plants that require such materials. BASF is the largest manufacturer of PIBs (10^6 metric tons $year^{-1}$ with costs ranging \$0.8 kg^{-1} for low $\overline{M_n}$ grades and \$1.7-2 kg^{-1} for medium to high $\overline{M_n}$ grades).[6] PIBs bearing a high (> 80 %) percentage of terminal unsaturation (reactive PIBs) are highly desirable but a cost effective, non-polluting system for their production has not been disclosed.[2f,7]

Butyl rubber (Figure 3) is a random copolymer isobutylene (98.5 mol %) with minor

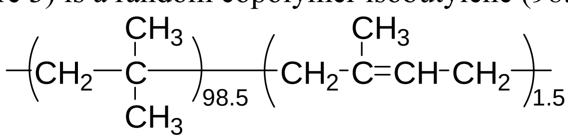

Figure 3

amounts of isoprene (1.5 mol %). Vulcanized butyl has the lowest gas and moisture permeability of all elastomers, excellent heat/ozone resistance, and high damping properties.[2d,i] The main use of butyl is in tire-curing bladders and inner tubes. Commercial processes for the manufacture of butyl are costly and detrimental to the environment as they operate at temperatures ≤ -100 °C and require the use of toxic methyl chloride.[2d-i] Currently > 760,000 metric tons of butyl is produced each year at a price of \$2.8-3 kg^{-1}.[1a,2f] Exxon and Lanxess are the major manufacturers of butyl rubber.

Polybutenes are ill-defined copolymers of isobutylene and minor amounts of 1-butene and Z/E 2-butenes.[2d,i] They are low molecular weight materials ($\overline{M_n}$ = 340-2200 g mol^{-1}) with viscosities ranging from 20 centistokes (cSt) to $7x10^4$ cSt and their primary application is as lubricants and viscosity modifiers.[2d,f] More than 750,000 metric tons of polybutenes are produced each year at an average cost of \$1 kg^{-1}.[2f] Production of high molecular weight polybutenes requires low temperatures and is costly. Polybutenes with high levels of terminal unsaturation are valuable in the production of lubrication additives but no cost effective and environmentally acceptable system exists for their production.[2f,7] Exxon, Amoco, BP, and BASF are major manufacturers of polybutenes.

Our Novel Polymerization Systems

Recently our research team developed a 2 component initiating system[3] that allows for the production of high molecular weight PIBs[8a] at elevated reaction temperatures (*e.g.* -60 °C) in the absence of solvent. The components of this system are of moderate to low cost and supported versions have also been tested. Supported versions in particular appear to have enhanced activity at higher reaction temperatures (*ca* -40 to -20 °C) and preliminary experiments indicate they will allow for the production of medium molecular weight PIBs at temperatures as high as 25 °C.[8b] Supported versions may also reduce post-polymerization purification steps by eliminating steps required for the removal of initiating components from the polymer and thereby reduce overall production costs. In many cases yields are high (*ca* 70 %) to almost quantitative. The uniqueness of this system offers the potential of generating new grades of butyl rubber that can be vulcanized using new chemistries that are not possible with traditional grades of butyl rubber. A final development is that our research team has discovered a potential green replacement for isoprene. This new comonomer is a cost effective and environmentally friendly replacement for isoprene and may enhance the production of butyl type rubber at elevated temperatures by moderating the polymerization process.[8c]

References

1. (a) Kirschner, M. *Chem. Market. Rep.*, **2005**, *June* 6-15, 34. (b) Blanchfield, L. *Icis Chem. Bus.*, **2006**, *Sept.* 4-10, 7. (c) Lim, J. *Icis Chem. Bus.*, **2007**, *July* 2-8, 6.
2. (a) Otto, M.; Müller-Cunradi, M. Ger. Patent 641,284 (1931). (b) Güterbock, H. *Polyisobutene*, Springer Verlag, Berlin, 1959. (c) Immel, W. *Polyisobutene* in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B.; Haskins, S.; Schulz, G. Eds.; VCH Publishers: Weinheim; 1992; Vol. A21, pp. 555-561. (d) Kennedy, J.P.; Marechal *Carbocationic Polymerization*, Wiley-Interscience, New York; 1982; Chap. 10. (e) Kresge, E. N.; Schatz, R. H.; Wang, H-C. *Isobutene polymers* in *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Elvers, B.; Haskins, S.; Schulz, G. Eds.; Wiley-Interscience: New York; 1987; Vol. 8, pp. 423-448. (f) Vairon, J. P.; Spassky, N. in *Cationic Polymerization*; Matyjaszewski, K. Ed.; Marcel Dekker: New York, 1996; p. 683-704. (g) Thomas, R. M.; Sparks, W. J. U.S. Patent 2,356,128 (1944). (h) Duffy, J.; Wilson, G.J. *Synthesis of butyl rubber by cationic polymerization* in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B.; Haskins, S.; Russey, W.; Schulz, G. Eds.; VCH Publishers: Weinheim; 1993; Vol. A23, pp. 288-294. (i) Duffy, J.; Wilson, G.J. *Halobutyl rubber* in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B.; Haskins, S.; Russey, W.; Schulz, G. Eds.; VCH Publishers: Weinheim; 1993; Vol. A23, pp. 314-318.
3. A provisional patent filing covering this technology is in progress.
4. (a) Kennedy, J. P. *Carbocationic Polymerization of Olefins*: *A Critical Inventory*; Wiley: New York, 1975; Ch 4. (b) Our technology makes use of other techniques besides reduced reaction temperature to reduce the extent of chain transfer.
5. Kennedy, J. P; Squires, R. G.. *Polymer*., **1965**, *6*, 579-587.
6. Marsalko, T. (BASF) *personal communication*, **2005**.
7. (a) Rath, H. P.; Hahn, D.; Sandrock, G.; Deyck, F.; Straeten, B. V.; Vree, E. D. US Patent 6,753,389 (2004). (b) Nolan, J. T., Jr.; Chafetz, H. US Patent 3,024,226 (1962). (c) Nolan, J. T., Jr.; Chafetz, H. US Patent 3,166,546 (1965). (d) Vierle, M.; Schön, D.; Bohnenpoll, M.; Kühn, F. E.; Nuyken, O. CA Patent 2,421,688 (2003). (e) Guerrero, A. Kulbaba, K. Bochmann, M. *Macromolecules* **2007**, *40*(12), 4124-4126.
8. (a) PIBs are used as a model for butyl rubber as both polymers exhibit similar molecular weight dependencies on temperature. In some cases molecular weights for PIBs prepared below -60 °C were so high they exceed the detection limits of the analytical equipment available. The unsupported system may be capable of generating commercially useful grades of butyl at temperatures as high as -40 to -20 °C. (b) The supported system was capable of producing PIBs with $\overline{M_n}$ > 20,000 g mol^{-1} at 25 °C but it should be noted that the reaction is exothermic and reaction temperature for these experiments most likely was > 50 °C. (c) It is believed that this green comonomer may aid in the production of high molecular butyl type polymers at elevated temperatures as it moderates the polymerization process and prevents violent exotherms that raise the reaction temperature rapidly.