© 2018 IJSRST | Volume 4 | Issue 8 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology

Enzymatic Functionalization Of Polyisobutylenes(Pib) Polymers

Prof. D. C. Patel
The H.N.S.B Ltd. Science College, Himatnagar, Gujarat, India

ABSTRACT

The aim of this research was to enzymatically functionalize Polyisobutylenes(PIB). The unique combination of properties including chemical/oxidative resistance, low Tg, hydrophobicity, biostability and biocompatibility renders polyisobutylene (PIB) an ideally suitable polymer for biomedical applications.(1,2) PIB-based amphiphilic networks, which are prepared by copolymerization of hydrophilic monomers including 2-hydroxyethyl methacrylate, N,N-dimethyl acrylamide, sulfoethyl methacrylate and 2-(dimethylamino)ethyl methacrylate with hydrophobic methacrylate-telechelic .PIB crosslinkers, have shown interesting properties for biomedical applications such as biocompatilibity, biostability, hemocompatibility, control of swelling by change in composition, controlled release of drugs and pH-sensitive swelling.(3,4,5)

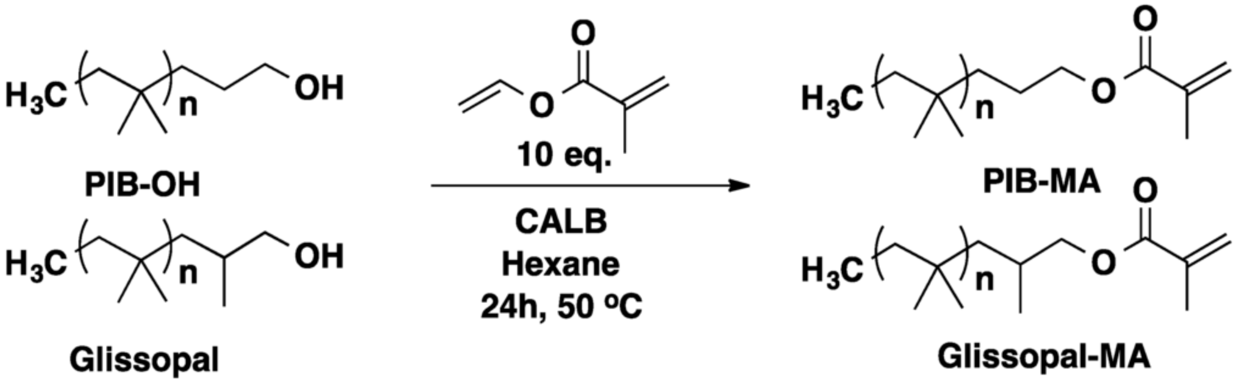
Keywords : Polyisobutylenes(PIB), hydrophobicity, hemocompatibility, copolymerization, methacrylate-telechelic, 2-hydroxyethyl methacrylate, biocompatilibity

I. INTRODUCTION

Linear triblock polystyrene-&-polyisobutylene-&-polystyrene (PS-&-PIB-&-PS; SIBS) and three-arm star PIB-(PS)3 block copolymers with about 10-40% PS displayed thermoplastic elastomeric (TPE) properties.(6,7) PIB-based TPEs are known to have good heat, environmental and chemical resistance, excellent barrier properties, and outstanding biostability and biocompatibility(8).SIBS recently received FDA approval for coating drug-eluting coronary stents and its uses for other biomedical applications such as ophthalmic implants and synthetic heart valves are currently under investigation.

II. Functionalization of Polyisobutylenes in Solution

The primary hydroxyl-functionalized polyisobutylenes, PIB-CH_2-CH_2-CH_2-OH (Mn = 5,800 g/mol, Mw/Mn = 1.09) and Glissopal-OH (PIB-CH_2-$CH(CH_3)$-CH_2-OH, Mn = 4,100 g/mol, Mw/Mn = 1.39), which were prepared via anti-Markovnikov hydrobromination of allyl-terminated PIB and Glissopal 2300 followed by hydrolysis,209 were reacted with about 10 equivalents of VMA. The polymer, PIB-CH_2-CH_2-CH_2-OH (0.4 g, 0.1 mmol, 0.02 mol/L) or Glissopal-OH(0.4 g, 0.1 mmol, 0.02 mol/L),was dissolved in hexane (5 mL) in a flask containing CALB (0.05 g, 3×10^{-4} mmol, 6×10^{-5} mol/L). The flask was sealed with a septum and purged with nitrogen. The reactions were started by the addition of VMA, 0.1 mL (0.8 mmol, 0.2 mol/L) and 0.14 mL (1.1 mmol, 0.2 mol/L), to PIB-CH_2-CH_2-CH_2-OH and Glissopal-OH solutions, respectively. After stirring the mixtures at 300 rpm for 24 hours at 50 °C, the enzyme was filtered; the polymers were precipitated into methanol and dried in a vacuum oven at room temperature.

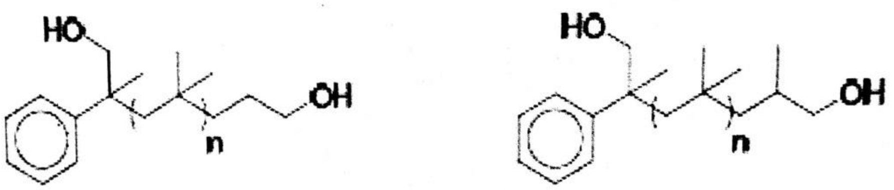


Functionalization of Polyisobutylenes in Bulk a-(tert.-Butyl)-ro-(2-chloro-2-methylpropyl)polyisobutylene (Mn = 1,500 g/mol,)

Mw/Mn = 1.29), which was synthesized via TMPCl/BCV initiated carbocationic polymerization of isobutylene, was converted to the corresponding hydroxyl-terminated polymer by dehydrochlorination followed by hydroboration/oxidation. Glissopal-OH was prepared from Glissopal 2300 by hydroboration/oxidation. These polymers were then enzymatically methacrylated.

Ten equivalents of vinyl methacrylate (0.2 mL, 1.4 mmol, 8.3 mol/L) was placed in a flask containing CALB (0.04 g, 2.3 x 10^{-4} mmol, 1.4 x 10^{-3} mol/L; 10 wt% relative to the total weight of reactants) and the hydroxyl-functionalized PIB (0.2 g, 0.1 mmol, 0.8 mol/L) derived from PIB-Cl. The flask was sealed, purged with nitrogen and the mixture was stirred at 300 rpm for 24 hours at 50 °C. After the reaction, the polymer was dissolved in hexane and the enzyme was filtered. The polymer was precipitated into methanol and dried in a vacuum oven at room temperature. Similarly, Glissopal-OH (0.4 g, 0.1 mmol, 0.8 mol/L) was reacted with 10 equivalents of vinyl methacrylate (0.1 mL, 1.1 mmol, 8.3 mol/L) in the presence of CALB (0.05 g, 3.1 x 10^{-4} mmol, 2.4 x 10^{-3} mol/L).

Regioselective Functionalization of Asymmetric a,o>(dihydroxyl)polyisobutylenes



The two asymmetric a,ro-hydroxyl-functionalized polyisobutylenes (Figure), HO-PIB-CH_2-CH_2-CH_2-OH and HO-PIB-CH_2-$CH(CH_3)$-CH_2-OH, the syntheses of Specifically, HO-PIB-CH_2-CH_2-CH_2-OH (0.3 g, 0.03 mmol, 0.009 mol/L, Mn =11,700 g/mol, Mw/Mn = 1.27) dissolved in hexane (3 mL) was placed in a round-bottom flask containing CALB (0.03 g, 1.9 x 10^{-4} mmol, 6.4 x 10^{-5} mol/L). Vinyl methacrylate (0.03 mL, 0.3 mmol, 0.1 mol/L) was added to this mixture. The flask was sealed and then purged with nitrogen. The solution was stirred at 300 rpm for 24 hours at 50 °C. After the reaction was complete the enzyme was filtered, the polymer was precipitated into methanol and dried in a vacuum oven at room temperature (yield: 0.2 g, conversion: 88.1%).

Similarly, HO-PIB-CH_2-$CH(CH_3)$-CH_2-OH (0.1 g, 0.02 mmol, 0.005 mol/L, Mn = 8,700 g/mol, Mw/Mn = 1.45) was reacted with vinyl methacrylate (0.03 mL, 0.2 mmol, 0.06 mol/L) in hexane (3.5 mL) in the presence of CALB (0.03 g, 2.1 x 10^{-4} mmol, 6.1 x 10^{-5} mol/L) (yield: 0.1 g, conversion: 85.7%).

III. REFERENCES

[1]. Puskas, J. E.; Kaszas, G. Carbocationic Polymerization. In Encyclopedia of Polymer Science and Technology, 3rd ed.; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 2003; Vol. 5, pp 382-418.

[2]. Kennedy, J. P. Designed rubbery biomaterials. Macromol. Symp. 2001, 175, 127¬131.

[3]. Ivan, B.; Kennedy, J. P.; Mackey, P. W. Controlled-release pharmaceuticals containing amphiphilic networks. U.S. Patent 5,073,381, 1991.

[4]. Keszler, B.; Kennedy, J. P. Amphiphilic networks. VII. Synthesis and characterization of pH-sensitive poly(sulfoethyl methacrylate)-polyisobutylene networks. J. Polym. Sci., Part A: Polym. Chem. 1994, 32, 3153-3160.

[5]. Chen, D.; Kennedy, J. P.; Kory, M. M.; Ely, D. L. Amphiphilic networks: II. Biocompatibility and controlled drug release of poly[isobutylene-co-2-(dimethylamino)ethyl methacrylate]. J. Biomed. Mater. Res. 1989, 23, 1327-1342.

[6]. Kennedy, J. P.; Puskas, J. E.; Kaszas, G.; Hager, W. G. Catalysts and solvents for the manufacture of polyisobutylene-based thermoplastic elastomers. U.S. Patent 4,946,899, 1990.

[7]. Kennedy, J. P.; Puskas, J. E.; Kaszas, G.; Hager, W. G. Manufacture of isobutylene-based thermoplastic elastomer block copolymers. PCT Int. Appl. 9511468, 1991.

[8]. Puskas, J. E.; Antony, P.; Kwon, Y.; Paulo, C.; Kovar, M.; Norton, P. R.; Kaszas, G.; Altstadt, V. Macromolecular engineering via carbocationic polymerization: branched structures, block copolymers and nanostructures. Macromol. Mater. Eng. 2001, 286, 565-582.