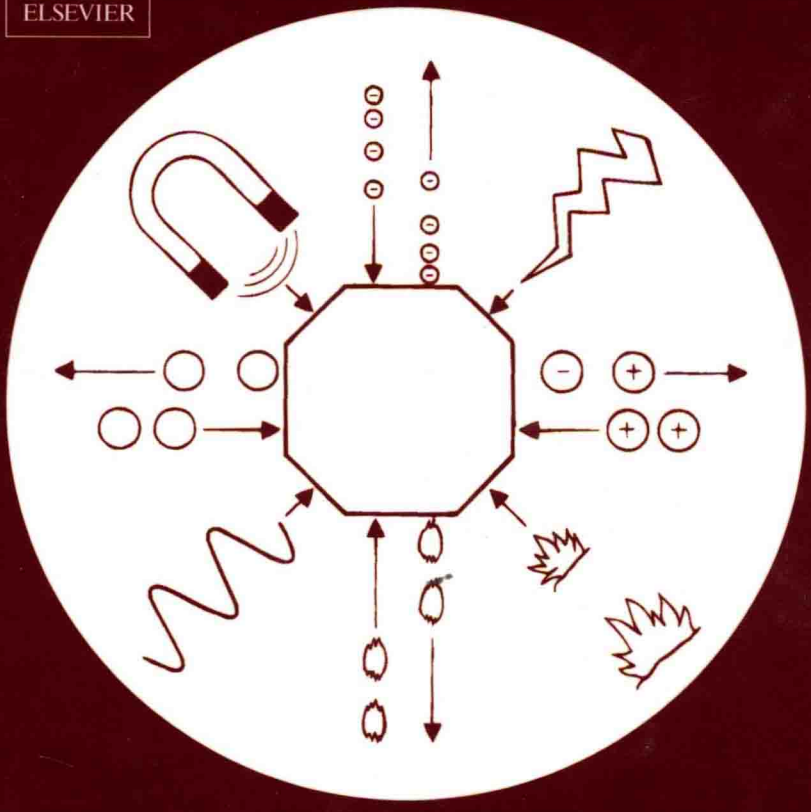
studies in surface science and catalysis



161

PROGRESS IN OLEFIN POLYMERIZATION CATALYSTS AND POLYOLEFIN MATERIALS

Takeshi Shiono
Kotohiro Nomura
Minoru Terano
(editors)

Studies in Surface Science and Catalysis

Advisory Editors: B. Delmon and J.T. Yates
Series Editor: G. Centi

Vol. 161

PROGRESS IN OLEFIN POLYMERIZATION CATALYSTS AND POLYOLEFIN MATERIALS

Proceedings of the First Asian Polyolefin Workshop, Nara, Japan, December 7-9, 2005

Edited by

Takeshi Shiono
Graduate School of Engineering, Hiroshima University
Higashi-Hiroshima, Japan

Kotohiro Nomura
Nara Institute of Science and Technology
Nara, Japan

Minoru Terano
Japan Advanced Institute of Science and Technology
Ishikawa, Japan

ELSEVIER

Amsterdam – Boston – Heidelberg – London – New York – Oxford – Paris
San Diego – San Francisco – Singapore – Sydney – Tokyo

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK

First edition 2006

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN-13: 978-0-444-52751-6
ISBN-10: 0-444-52751-6
ISSN (Series): 0167-2991

Printed and bound in The Netherlands

06 07 08 09 10 10 9 8 7 6 5 4 3 2 1

Studies in Surface Science and Catalysis 161

PROGRESS IN OLEFIN POLYMERIZATION CATALYSTS AND POLYOLEFIN MATERIALS

Committee

Academic
Lee, Dong-Ho (Kyunpook National University, Korea)
Li, Bo-Geng (Zhejiang University, PR China)
Noh, Seok Kyun (Yeungnam University, Korea)
Nomura, Kotohiro (Chair, NAIST, Japan, General Secretary)
Shiono, Takeshi (Chair, Hiroshima University, Japan)
Sun, Wen-Hua (Institute of Chemistry, CAS, PR China)
Terano, Minoru (Chair, JAIST, Japan)
Woo, Seong Ihl (KAIST, Korea)

Industry
Arai, Toru (Denka Co.)
Hujita, Takashi (Toho Catalyst Co., Ltd.)
Imuta, Jun-ichi (Mitsui Chemicals Inc.)
Kuramoto, Masahiko (Idemitsu Kosan Co., Ltd.)
Miyatake, Tatsuya (Sumitomo Chemical Co., Ltd.)
Takahashi, Mitsuru (Tosoh Finechem. Corp.)
Tayano, Takao (Japan Polypropylene Corp.)
Watanabe, Harumi (Asahi Kasei Chemicals Corp.)

Organized by
Catalysis Society of Japan, Polymerization Catalysis Division

Coorganized by
The Chemical Society of Japan
The Japan Petroleum Institute
The Society of Polymer Science, Japan
Nara Convention Bureau

Preface

More than a half-century has passed since the finding of Ziegler-Natta catalysts and a quarter-century from that of metallocene catalysts. The development of sophisticated production systems owing to the innovative catalyst technology has made polyolefin one of the most important polymer materials. Considerable research effort has been continuously paid on polyolefin technology in the world, and Asia has been growing up as one of the most active regions in this field. Asian Polyolefin Workshop (APO) was thus planned to provide a venue for Asian scientists and engineers identifying and exploring the areas of common interests.

The 1st APO was held in Nara on December 7th – 9th, 2005, with more than 100 participants from China, Israel, India, Japan, Korea, Russia, Spain and Thailand. The workshop concerned the following research topics with 34 oral and 37 poster presentations;

1) Heterogeneous olefin polymerization catalysts
   Traditional Ziegler-Natta, Phillips, heterogenized metallocene and post metallocenes
2) Homogeneous olefin polymerization catalysts
   Traditional Ziegler-Natta, metallocene and post metallocenes
3) Precise synthesis of new polyolefins
4) Structure and properties of polyolefins
5) Engineering aspects of olefin polymerization

This book is a collection of the important papers presented at the Workshop.

We believe that these works will stimulate further research as well as contribute to an understanding of the activity of Asia in this field.

April, 2006

Takeshi Shiono
Kotohiro Nomura
Minoru Terano
Editors

Contents

Progress in Olefin Polymerization Catalysts and Polyolefin Materials
T. Shiono, K. Nomura and M. Terano (Editors)

1

Creation of New Polyolefin Hybrids on the Surface of Molded Polypropylene Sheet

Shingo Matsuo*, Tomoaki Matsugi, Junji Saito, Nobuo Kawahara, Hideyuki Kaneko, Norio Kashiwa

R&D Center, Mitsui Chemicals, Inc., 580-32, Nagaura Sodegaura, Chiba, 299-0265, Japan

Abstract Surface polymerization of 2-hydroxyethyl methacrylate (HEMA) at the initiation sites on the molded sheet of polypropylene macroinitiator (PP-MI) was performed by a CuBr mediated controlled radical polymerization (CRP). The obtained sheet was coated with poly(HEMA), then analyzed by attenuated total reflection infrared (ATR/IR) and transmission electron microscopy (TEM) to investigate the structure and the morphology. It was revealed that PP-graft-poly(HEMA) was successfully synthesized on the sheet and showed unique morphological features.

1. INTRODUCTION

Polyolefins (POs) are the most widely used commercial polymers. On the other hand, it is becoming important to add new functions into POs in order to broaden the applications vis-a-vis certain highly valuable fields. One approach to develop this point that has been attracting much attention is the creation of hybrid materials having chemical linkage between PO and non-PO [1]. In order to produce these materials, it is necessary to apply either PO macroinitiator [2,3,4], PO macromonomer [5,6] or reactive PO [7]. By doing so, it is possible to create a new class of PO/non-PO hybrid polymers possessing unique topologies, compositions and properties.

Recently, some methods have been developed for introduction of functional groups into PO, for example, copolymerization of olefin and polar monomers [2,8,9]. This functional PO was useful to create PO macroinitiator for controlled radical polymerization (CRP). It has already been reported in our

previous paper [3] that the method to produce polyethylene-block-poly(methyl methacrylate) block copolymers under solution conditions is by using terminally esterified polyethylene as a PO macroinitiator. But to produce PO-block or graft-non-PO copolymers like that on molded sheet has not yet been reported. In this paper, we would like to report the CRP of 2-hydroxyethyl methacrylate (HEMA) to prepare PP-graft-poly(HEMA) on a molded sheet of PP-MI by using PO macroinitiator techniques and the results of surface observations.

2. EXPERIMENTAL

Typical example for synthesis of polypropylene macroinitiator (PP-MI) Toluene (1 500 mL) was introduced into 2 000-mL glass flask equipped with a mechanical stirrer, a condenser, and a thermometer under nitrogen. After the solvent was thermostated to 40°C, then propylene gas was fed (100 L/h) for 20 min, triisobutylaluminium (44 mmol) and 10-undecen-1-ol (40 mmol) were added to the reactor. Pretreated solution of rac-ethylenebis(indenyl)zirconium dichloride ($Et(Ind)_2ZrCl_2$, 0.020 mmol) and methylaluminoxane (MAO, 4.0 mmol) in 10 ml toluene for 5 min was added to start polymerization. The polymerization was conducted for 20 min under vigorous stirring (600 rpm). Isobutyl alcohol (10 mL) was added to terminate the polymerization. The resulting solution was poured into methanol (3 000 mL) with concentrated HCl (5 mL) to precipitate the copolymer. The resulting polymer was collected by filtration, washed with methanol (300 mL x3), and dried under vacuum. Thus 53.6 g of isotactic poly(propylene-*co*-10-undecen-1-ol) was obtained as white powder (M_n: 15 400). ^{1}H NMR analysis revealed that 1.0 mol% of 10-undecen-1-ol was incorporated into the copolymer.

The resulting poly(propylene-*co*-10-undecen-1-ol) (50 g, 12 mmol of OH group), triethylamine (72 mmol), 2-bromoisobutyryl bromide (60 mmol), and hexane (600 mL) were added to a 1 000 mL-glass flask equipped with a mechanical stirrer, a condenser, and a thermometer under nitrogen. The mixture was heated to 80 °C and stirred for 80 min. Then, the reaction mixture was cooled to room temperature. The precipitated polymer was collected by filtration, washed with methanol, 1N HCl (aq), and dried at 50 °C under vacuum. Thus, esterified PP as a macroinitiator was obtained in quantitative yield.

Typical example for controlled radical polymerization (CRP) on the surface of PP-MI sheet A typical CRP was performed as follows. A PP-MI sheet (ca. 1 mm of thickness) prepared by hot-pressing method at 180 °C (10 Mpa, 1 min) was set into 500-mL flat-bottomed glass flask equipped with a

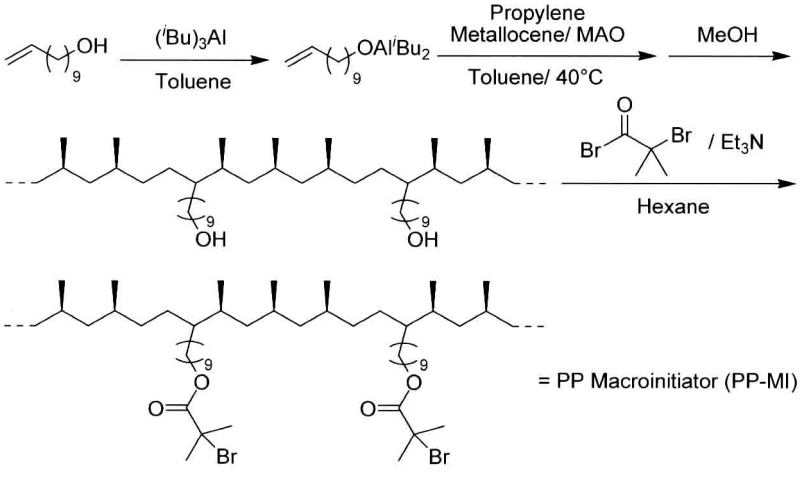
magnetic stirrer. Dried ethanol (250 mL) and 2-hydroxyethyl methacrylate (HEMA, 50 mL) were added to the flask under nitrogen atmosphere and stirred for 20 min at 25 °C. Ethanol and HEMA were degassed by bubbling with nitrogen for 30 min prior to use. CuBr (5.3 mmol) and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 10.6 mmol) were dissolved in ethanol (5 mL) and stirred for 5 min, then the solution was added into the flask to initiate the polymerization. The polymerization was conducted with stirring at 25 °C. After the desired polymerization time, the polymerization was stopped, and the resulting sheet was washed in excess methanol. The sheet was dried at 80 °C under vacuum.

3. RESULTS AND DISCUSSION

3.1. Preparation of polypropylene macroinitiator

A synthetic route for preparation of polypropylene macroinitiator (PP-MI) is shown in Scheme 1. Hydroxylated PP was prepared by copolymerization of propylene and 10-undecen-1-ol with $Et(Ind)_2ZrCl_2$/MAO at 40 °C. Triisobutylaluminium was used as a reagent for masking hydroxyl group of 10-undecen-1-ol. The resulting polymer solution was treated with acidic methanol to remove catalyst residues and aluminum moiety which caused gel formation. The thus obtained hydroxylated PP was treated with 2-bromoisobutyrylbromide and triethylamine in hexane at 80 °C to produce esterified PP, which was able to work as a macroinitiator (i.e. PP-MI) for CRP. This PP-MI was molded by hot-pressing (ca. 1 mm of thickness) at 180 °C.

Scheme 1. Preparation of PP Macroinitiator



3.2. Controlled radical polymerization on the surface of PP sheet

The presence of initiation sites exposed on the surface was confirmed by attenuated total reflection infrared (ATR/IR) analysis. CRP of HEMA on the surface of PP-MI sheet was conducted at 25°C in ethanol for 24 h. The surface of the sheet was obviously changed to rough and opaque after CRP, then it was analyzed by ATR/IR and transmission electron microscope (TEM) in detail.

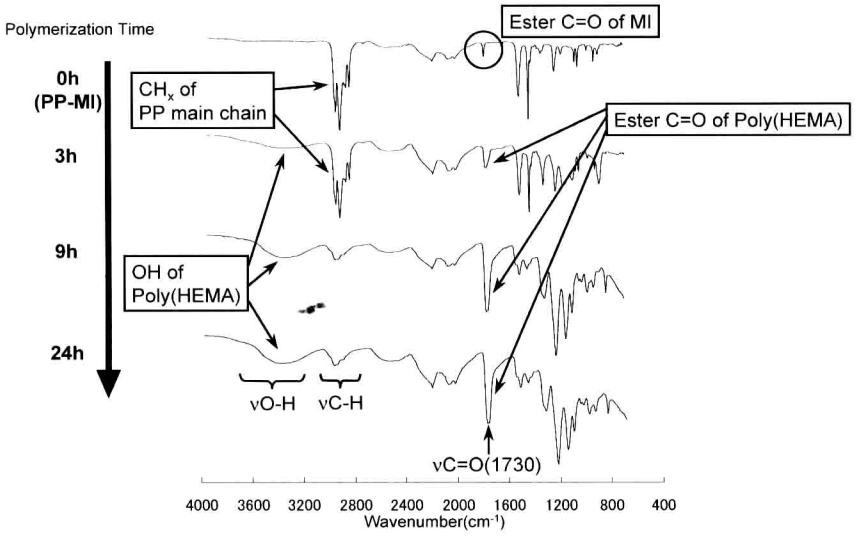


Figure 1. ATR/IR spectra on the surface of PP-MI sheet

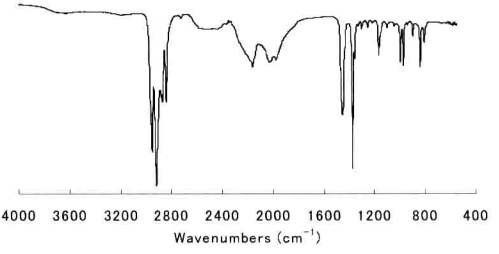


Figure 2. ATR/IR spectrum on the surface of homo PP sheet after treated under the same conditions as CRP

Figure 1 shows the change of ATR/IR spectra on the surface of the sheet. As the polymerization advanced, the absorption of the hydroxyl group and the carbonyl group derived from the poly(HEMA) became stronger with