Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Notes Copolymerization of Propylene with Acrylonitrile or Methyl Acrylate Using Et(Ind)$_2$ZrCl$_2$/MAO or Et(H$_4$Ind)$_2$ZrCl$_2$/MAO Catalyst System

D. Chandrika Mudalige[a]; G. L. Rempel[a]
[a] Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

To cite this Article Mudalige, D. Chandrika and Rempel, G. L.(1997) 'Notes Copolymerization of Propylene with Acrylonitrile or Methyl Acrylate Using Et(Ind)$_2$ZrCl$_2$/MAO or Et(H$_4$Ind)$_2$ZrCl$_2$/MAO Catalyst System', Journal of Macromolecular Science, Part A, 34: 2, 361 — 368

To link to this Article: DOI: 10.1080/10601329708014961

URL: http://dx.doi.org/10.1080/10601329708014961

J.M.S.—PURE APPL. CHEM., A34(2), pp. 361-368 (1997)

NOTES

COPOLYMERIZATION OF PROPYLENE WITH ACRYLONITRILE OR METHYL ACRYLATE USING $Et(Ind)_2ZrCl_2$/MAO OR $Et(H_4Ind)_2ZrCl_2$/MAO CATALYST SYSTEM

D. Chandrika Mudalige and G. L. Rempel
Department of Chemical Engineering, University of Waterloo,
Waterloo, Ontario N2L 3G1, Canada

ABSTRACT

Copolymerization of propylene with acrylonitrile (AN) or methyl acrylate (MA) catalyzed by $Et(Ind)_2ZrCl_2$ **(1)**/MAO or $Et(H_4Ind)_2ZrCl_2$ **(2)**/MAO resulted in polypropylene homopolymer with zero incorporation of either of the comonomer. However, use of Et_2AlCl or $AlMe_3$ with the zircononcene catalysts resulted in some incorporation of the comonomer into polypropylene, but in amounts negligible to cause a significant change in the yield and properties (tacticity and melting point) of the copolymer compared to those of polypropylene obtained under identical conditions.

INTRODUCTION

Polypropylene (PP) copolymers are economically important because they can be produced with an unique balance of properties which can be tailored for specific applications. In many applications the presence of polar functional groups attached to polyolefins imparts useful properties. For example, the polar groups may supply surface activity for surfactants, adhesives or corrosion inhibitors. Additionally, these polar functionalities may be used as means of adding further groups to, and/or cross linking the polymer. Furthermore, a copolymer comprised of

propylene and acrylonitrile could be an important substitute for hydrogenated nitrile butadiene rubber (HNBR) which has many commercial applications [1]. HNBR is currently produced by a two step process whereby butadiene and acrylonitrile are first copolymerized and then the copolymer is catalytically hydrogenated [2].
Since the advent of polyolefin synthesis using metallocene technology many attempts have been made in the use of metallocene catalysts in functionalized polyolefin production. All such attempts were aimed at overcoming the common problem of catalyst deactivation by the functional monomers; stable complex formation between the active catalyst center and the hetero-atom of the functional monomers cause inhibition of the polymerization reaction [3]. Attempts made at overcoming this include, the use of vinyl monomers with functional groups that are distant and hence unconjugated to the double bond [4], use of functional monomers bearing sterically hindered hetero-atoms[5], and the use of borane monomers [6]. Recently, cationic group 4 metallocene catalysts have been successfully used in homopolymerization of functionalized vinyl monomers [7], and the use of a Pd(II) catalyst in copolymerization of ethylene or propylene with alkyl acrylates is also reported [8] Precomplexed functional monomers have also been used in the past with limited success in transition-metal catalyzed polymerization reactions.[9] The past work is mainly involved with the use of conventional Ziegler-Nata catalysts in homo- and copolymerization of aluminum alkyl-complexed functional monomers. Due to our interest in $Et(Ind)_2ZrCl_2$ **(1)**/MAO and $Et(H_4Ind)_2ZrCl_2$ **(2)**/MAO catalyst systems [10] and our ongoing research on HNBR production, [11] we became interested in re-visiting the precomplexed monomer approach in metallocene catalyzed propylene-acrylonitrile copolymerization. Propylene-methyl acrylate copolymerization was also studied for comparison. In this paper we wish to report the attempted copolymerization of propylene with precomplexed acrylonitrile (AN) or methylacrylate (MA) using $Et(Ind)_2ZrCl_2$ (**1**)/MAO or $Et(H_4\text{-}Ind)_2ZrCl_2$ (**2**)/MAO catalyst systems. The aluminum alkyls Et_2AlCl or $AlMe_3$ were used in precomplexation of the polar monomers.

EXPERIMENTAL

Materials: Acrylonitrile (Aldrich) was dried over $CaCl_2$ and CaH_2 respectively, and distilled under vacuum. Methyl acrylate (Aldrich) was washed with 10%

sodium hydroxide solution, dried over anhydrous $MgSO_4$ and distilled under vacuum. The Al-alkyls Et_2AlCl (1.8 M in toluene) and $AlMe_3$ (2.0 M in hexanes) were used as supplied from Aldrich. Propylene (C.P. grade) was purified by passing through molecular sieves and oxygen scavengers. Freshly distilled toluene over sodium/benzophenone was used in all reactions. Methylalumoxane (MAO) was purchased from Albemarle as a 10 wt.-% solution in toluene. The zirconocenes $Et(Ind)_2ZrCl_2$ and $Et(H_4Ind)_2ZrCl_2$ were synthesized by published methods.[12] Precomplexation of AN and MA was achieved by mixing an equimolar ratio of Et_2AlCl or $AlMe_3$ with either of the monomers.

Polymerization reactions: The polymerizations were carried out in a three-necked flask equipped with a condenser, and a propylene inlet. The third neck was capped with a rubber septum which was used for addition of solvent, catalyst solution, and the liquid monomers into the flask. The condenser was connected to an oil-bubbler and to the vacuum line via a 3-way tap, and the whole system was evacuated and purged with nitrogen three times at 70-80 °C. After cooling the flask to room temperature freshly distilled toluene is cannula transferred under nitrogen, and the solvent is saturated with propylene over a period of 15-30 min at room temperature. The metallocene/MAO solution is then injected into the flask, propylene polymerization was started first, and the comonomer/Al-alkyl adduct is injected after five minutes. After 4 h, CH_3OH (4-5 mL) was added slowly to quench the reaction, and the mixture is poured into acidic CH_3OH solution (600 mL CH_3OH containing 2 mL of HCl). After stirring overnight, the polymer was filtered and dried under vacuum at 60-70 °C for 24 h.

Polymer characterization: IR spectra were recorded using a Nicolet 520 FTIR spectrometer. Samples were prepared by compressing a mixture of PP with KBr at room temperature. Polymer isotacticities, measured as the [mmmm] pentad content, were determined by FTIR spectroscopy, [13] and the calculations were done as proposed by Chien *et al.* according to the following equation. [14]

$$A_{998}/A_{973} = (0.864 \pm 0.004)[mmmm] + 0.10$$

The melting temperatures (T_m) of PP samples were measured on a DSC 2920 differential scanning calorimeter (TA Instruments) using a sample of about 5 mg

and a heating rate of 20 °C/min. T_m was obtained from the second scan after complete melting and cooling of the samples.

RESULTS AND DISCUSSION

An attempted copolymerization of propylene with AN or MA using $Et(Ind)_2ZrCl_2$ (1)/MAO or $Et(H_4Ind)_2ZrCl_2$ (2)/MAO catalyst systems produced disappointing results. No polymerization was observed in the experiments carried out having both propylene and AN (or MA) in solution prior to the addition of the catalyst. The experiments where the polar monomer was added after initiating propylene homopolymerization resulted only in polypropylene homopolymer. In the latter experiments, addition of the polar monomers caused complete quenching of polymerization reaction which was evident from the lack of propylene uptake. These results were not surprising due to the known intolerance of these metallocene catalyst systems to most polar functional groups such as ethers, esters, amines, alcohols, and carboxylic acids; the possible cause is proposed to be formation of stable complexes between the catalytically active cationic metallocene centers and the polar monomers which hinders the access of propylene to the catalytic site.[3] In an attempt to overcome this problem the use of preformed Lewis acid-base complexes of AN and MA where the polar functionalities are blocked by complex formation with the Lewis acid is studied in the present work. The Lewis acids Et_2AlCl and $AlMe_3$ were used for this purpose, and the choice of the Lewis acid was made such that it causes minimal effect to the metallocene/MAO catalyst system. The copolymerization experiments were carried out with (1)/MAO or (2)/MAO catalysts, and with each catalyst system homopolymerization of propylene was carried out for five minutes prior to the addition of Lewis acid-MA or Lewis acid-AN adduct to the reaction mixture. The total reaction time of each experiment was 4 h after which the reaction is quenched and the polymer is precipitated by the addition of methanol to the medium. The results obtained for a series of such experiments are summarized in Table 1, and the results obtained

TABLE 1: Copolymerization of propylene with methyl acrylate or acrylonitrile using $Et(Ind)_2ZrCl_2$ (1)/MAO or $Et(H_4Ind)_2ZrCl_2$ (2)/MAO catalyst system.[a]

Exp #	Al-alkyl[b]	Catalyst	Wt. of polymer obtained (g)	presence of ν_{CN} or ν_{CO} in IR	% [mmmm]	T_m °C
with acrylonitrile[c]						
1	$AlEt_2Cl$	2	0.37	yes	76.0	133.6
2	$AlMe_3$	2	0.35	yes	74.5	136.0
3	$AlEt_2Cl$	1	3.20	yes	76.6	137.9
4	___	1	2.90	no	80.9	137.7
with methyl acrylate[d]						
5	$AlMe_3$[e]	2	0.35	yes	70.8	136.1
6	___	2	0.39	no	74.4	137.9

[a] reaction conditions: metallocene = 8.21×10^{-6} mol; MAO = 8.62×10^{-3} mol; toluene = 100 mL; temperature (T_p) = 20-22 °C; $p(C_3H_6)$ = 1 atm. [b] R_nAlCl_{3-n} = 1.08×10^{-2} mol, used in precomplexation of the comonomers. [c] AN = 9.42×10^{-3} mol. [d] MA = 7.77×10^{-3} mol. [e] $AlMe_3$ = 8.0×10^{-3} mol.

with un-complexed polar monomers are also included (entries 4 and 6) for comparison.

A drastic decrease in catalyst activity was observed immediately upon addition of the polar monomer-Lewis acid adduct to the system, which was evident from the marked decrease in the propylene uptake. The propylene uptake decreased from its maximum to near zero within 30 minutes in all the experiments. In order to compare the results of these copolymerization reactions, a set of blank experiments were carried out under identical conditions where propylene homopolymerization was studied for 4 h, and 5 min reaction time intervals, respectively (Table 2).

TABLE 2: Propylene polymerization catalyzed by $Et(Ind)_2ZrCl_2$ (1)/MAO or $Et(H_4Ind)_2ZrCl_2$ (2)/MAO catalyst system.[a]

Exp #	Catalyst	Reaction time	Wt. of polymer obtained (g)	% [mmmm]	T_m °C
1	2	4 h	27.50	85.3	130.3
2	1	4 h	35.70	82.0	130.3
3	2	5 min	0.40	78.2	136.2
4	1	5 min	3.40	76.3	137.7

[a] The reaction conditions are same as in Table 1.

From a comparison of the weights of the resulting polymers in Table 1 with those in Table 2 it is clear that copolymerization experiments had lasted only for five minute time period. The apparent propylene uptake upto a total of 30 minutes could be due to increased propylene solubility in the medium; addition of AN- or MA-Lewis acid adduct results in an exotherm. Thus it is clear that the addition of the polar-monomer/Lewis acid adduct had essentially quenched the polymerization reaction. However, the IR spectra of the resulting polymers do show incorporation of AN or MA, whereas no incorporation of either of the comonomer was seen when uncomplexed MA or AN was used (Table 1). As the observed IR data of the former could also be a result of having the comonomer adsorbed onto polypropylene, the copolymers were repeatedly washed, and extracted with methanol under reflux temperature and filtered hot. The IR spectra of the resulting polymers show ν_{CN} (at 2232 cm^{-1}) and ν_{CO} (at 1740 cm^{-1}) bands with roughly the same intensities prior to the work-up procedure. Thus it is clear that the products are copolymers. However, from a comparison of the data in Table 1 and Table 2 it is clear that the properties of the copolymers (tacticity and melting point) are almost identical to those of polypropylene obtained in 5 min reaction time period (entries 3 and 4 in Table 2). Thus it could be concluded that incorporation of MA or AN to polypropylene has not occurred to an appreciable extent so as to cause a significant change in tacticity and melting point of the polymer.

CONCLUSION

The attempted copolymerization of propylene with Lewis acid-complexed MA or AN was presented in this paper. This approach seems to lead to some incorporation of the polar monomers into polypropylene. However, the amount incorporated was not significant so as to cause an appreciable change in the properties of the copolymer compared to those of polypropylene obtained under identical conditions.

ACKNOWLEDGMENTS

Financial support of this research by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1. a) Yu. S. Kovshov, V. V. Moiseev, T. P. Zhasrkikh, and I. P. Zornokov, *Int. Polym. Sci. Technol.* 18(2), T6 (1991). b) S. Bhattacharjee, A. K. Bhowmick, and B. N. Avasthi, "*Elastomer Technolgy Handbook*", pp 519-556, CRC Press, Boca Raton, FL, 1993.
2. D. Oppelt, H. Schuster, J. Thormer, and R. Braden, *British Pat.* 1 558 491 (1976); *German Pat.* DE 2 539 132; CA 87: 168798 m.
3. J. Boor Jr., "Ziegler-Natta Catalysts and Polymerizations", Academic Press, New York, 1979.
4. a) T. C. Chung, *Macromolecules* 21, 865 (1988). b) M. R. Kesti, G. W. Coates, and R. M. Waymouth, *J. Am. Chem. Soc.* 114, 9679 (1992). c) T. C. Chung, and D. Rhubright, *Macromolecules* 26, 3019 (1993).
5. Some representative examples include: a) A. R. Padwa, *Prog. Polym. Sci.* 14, 811 (1989). b) L. M. Landoll, and D. S. Breslow, *J. Polym. Sci., Part A:*

Polym. Chem. **27**, 2189 (1989). c) M. D. Purgett, and O. Vogl, *ibid* **27**, 2051 (1989). d) D. N. Schulz, and J. Bock, *J. Macromol. Sci., Chem.* **A28**(11-12), 1235 (1991). e) C. E. Wilen, M. Auer, and J. H. Nasman, *J. Polym. Sci., Part A: Polym. Chem.* **30**, 1163 (1992).

6. a) T. C. Chung, *Macromolecules* **21**, 865 (1988). b) T. C. Chung, and D. Rhubright, *ibid* **26**, 3019 (1993).
7. a) M. R. Kesti, G. W. Coates, and R. M. Waymouth, *J. Am. Chem. Soc.* **114**, 9679 (1992). b) K. M. Stein, M. R. Kesti, G. W. Coates, and R. M. Waymouth, *Polym. Prepr.* **35**(1), 480 (1994). c) H. Deng, T. Shiono, and K. Soga, *Macromolecules* **28**, 3067 (1995).
8. L. K. Johnson, S. Mecking, and M. Brookhart, *J. Am. Chem. Soc.* **118**, 267 (1996).
9. a) K. J. Clark, and W. G. City, *U.S. Pat.* 3 492 277 (1970). b) K. Tanaka, T. Iwata, and J. Sasaki, *Jap. Pat.* 73 37, 755(1973) and *Jap. Pat.* 73 7, 756 (1973). c) C. Carlini, *J. Polym. Sci., Polym. Chem. Edn.* **18**, 799 (1980). d) M. D. Purgett, and O. Vogl, *J. Macromolec. Sci.* **A24** 1465 (1987).
10. a) J. Huang, Ph. D. Thesis, University of Waterloo, 1995. b) J. Huang, and G. L. Rempel, *Prog. Polym. Sci.* **14**, 459 (1995). c) J. Huang, and G. L. Rempel, submitted to *Ind. Eng. Chem. Res.* June (1996).
11. a) G. L. Rempel, N. T. McManus, and N. A. Mohammadi, *U.S. Pat.* 5 057 581 (1991); CA 116: 42943d. b) N. T. McManus, and G. L. Rempel, *U.S. Pat.* 5 075 388 (1991); CA 116: 130954p. c) X. Y. Guo, and G. L. Rempel, *Stud. Surf. Sci. Catal.* **73**, 135 (1992). d) N. T. McManus, and G. L. Rempel, *Rev. Macromol. Chem. Phys.* **C35**(2), 239 (1995).
12. a) F. R. W. P. Wild, L. Zsolnai, G. Huttner, and H. H. Brintzinger, *J. Organomet. Chem.* **232**, 233 (1982). b) F. R. W. P. Wild, M. Wasincionek, G. Huttner, and H. H. Brintzinger, *ibid* **288**, 63 (1985). c) S. Collins, B. Kuntz, N. J. Taylor, and D. G. Ward, *ibid* **342**, 21 (1988).
13. D. R. Burfield, and P. S. T. Loi, *J. Appl. Polym. Sci.* **36**, 279 (1988).
14. J. C. W. Chien, B. Rieger, and H. M. Herzog, *J. Polym. Sci., Polym. Chem. Ed.* **28**, 2907 (1990).