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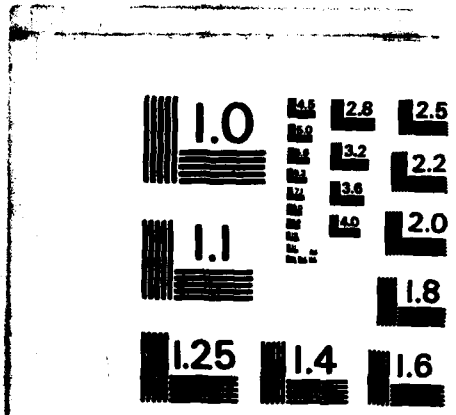

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OFFICE OF NAVAL RESEARCH
Contract N00014-77-C-0311
Task No. NR 356-646

TECHNICAL REPORT NO. 14

Synthesis and Characterization of a 1,4 Polybutadiene/Isotactic Polypropylene Block Copolymer

by

M.A. Drzewinski and R.E. Cohen
MIT Department of Chemical Engineering
Cambridge, MA 02139

November 19, 1984

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A148 199 / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis and Characterization of a 1,4 Polybutadiene/Isotactic Polypropylene Block Copolymer	5. TYPE OF REPORT & PERIOD COVERED Technical Report 6. PERFORMING ORG. REPORT NUMBER 14
7. AUTHOR(s) M.A. Drzewinski and R.E. Cohen	8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0311
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemical Engineering Massachusetts Institute of Technology Cambridge, MA 02139	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR356646
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy St., Arlington, VA 22217	12. REPORT DATE November 19, 1984 13. NUMBER OF PAGES 6
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report) 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES
To appear in the ACS Division of Polymeric Materials Science and Engineering preprints, Spring 1985.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
block copolymers
transformation reactions
semicrystalline block copolymer
anionic polymerization
Ziegler-Natta polymerization
isotactic polypropylene modifier

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Based on the nature of the anionic-to-Ziegler Natta transformation reaction employed, the subsequent fractionation and characterization of the product, and particularly the transmission electron microscopy of the morphology of the polymer produced, it is concluded that a 1,4 polybutadiene/isotactic polypropylene diblock copolymer has been produced. Certain properties and potential uses of this copolymer are discussed in this preliminary report.

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S/N 0102-014-6601

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SYNTHESIS AND CHARACTERIZATION OF A 1,4 POLYBUTADIENE/ISOTACTIC POLYPROPYLENE BLOCK COPOLYMER.

M. A. Drzewinski and R. E. Cohen
MIT Department of Chemical Engineering, Cambridge, MA 02139.

INTRODUCTION

The inherent "living" nature of anionic polymerization makes it the method of choice for the preparation of block copolymers, particularly when well defined structures are required. The anionic mechanism is not suitable for the polymerization of stereoregular olefinic polymers and therefore the preparation of block copolymers containing crystalline olefinic sequences has been extremely limited.

In this study, an alternative synthetic method has been used to prepare a novel block copolymer of 1,4 polybutadiene and isotactic polypropylene. In addition to presenting details of the synthesis, this paper will emphasize the importance of molecular and morphological characterization in verifying the block nature of such materials.

EXPERIMENTAL

Materials: All chemical reagents and monomers were extensively purified by methods usually employed for anionic and/or coordination polymerizations.(1)

Synthesis: The polymerizations were performed in a thick walled Pyrex reactor fitted with Teflon connections at all ports. The design and use of the reactor apparatus are described fully elsewhere.(1)

The reaction was begun by adding n-butyl lithium (nBuLi) to "living" gel purified (2) hexane (50°C). Liquid butadiene monomer (0°C) was then added so as to maintain a controlled reactor pressure of less than 1000 mm Hg. The extent of reaction was monitored barometrically until a 98 - 99% conversion was reached. At this time, a 1.0 ml. aliquot of the faint yellow living polybutadiene solution was removed from the reactor by syringe to obtain a molecular weight by GPC. The extent of reaction was thus checked to be certain that the vast majority of butadiene monomer had been consumed. The reactor was then evacuated and flushed with ultra-high purity argon while being cooled to 0°C. Titanium tetrachloride ($TiCl_4$) was added quickly with vigorous stirring so that a Li/Ti ratio between 2 to 3 and overall Ti concentration between 10^{-2} to 10^{-3} moles/liter was obtained. The reactor was again brought up to 50°C and evacuated.

Propylene gas was then added at a rate so as to maintain a pressure of 900 mm Hg. Within twenty minutes after the addition of propylene, a noticeable insoluble polymer fraction began to develop in the reactor. Two hours after the additon of propylene, the reactor pressure was increased to 950 mm Hg and the reactor was then sealed off. The reactor pressure drop was monitored while the polymerization continued. Fifteen hours after the initial addition of propylene, the reaction was terminated by the addition of a 5% solution of HCl in ethanol.

The reaction mixture was allowed to stir for one hour under inert conditions. The insoluble polymeric precipitate, hereafter referred to as the original block material, was washed several times with ethanol and then dried in vacuum at 25°C. The soluble polymer obtained from the reactor was precipitated into ethanol and this polymeric material, hereafter referred to as the polybutadiene fraction, was also washed and dried.

Polymer Purification: The reaction products described above were subjected to basic characterization before any further purification was performed (see below). The polybutadiene fraction showed no signs of polypropylene (IR or NMR) and had a composition of 66% cis 1,4; 27% trans 1,4; and 7% 1,2 polybutadiene. The GPC molecular weight (calibrated with polybutadiene standards) of the polybutadiene fraction was similar to that of the aliquot taken during the reaction (M = 5000; Mw/Mn = 1.2).

The original block material contained about 75% polybutadiene and 25% isotactic polypropylene (IR). Selective extractions with 2-pentanone, hexane and p-xylene resulted in a p-xylene soluble fraction, hereafter referred to as the soluble block material, with an overall composition of 40% 1,4 polybutadiene and 60% isotactic polypropylene.

Molecular and Morphological Characterization: In order to substantiate the block copolymer nature of the product, the materials of this synthesis were subjected to a large number of tests including: IR, NMR, GPC, DSC, SEM, TEM and optical microscopy. The details of these tests will be published elsewhere.(3)

RESULTS AND DISCUSSION

Although aluminium alkyls are preferred, lithium alkyls are also capable of forming coordination catalysts. The extension of this to polymeric lithium alkyls has been demonstrated.(4) The still further assertion that these systems (living anionic polymer + transition metal salt + second monomer) can lead to the formation of block copolymers is supported by the fact that the alkylating species attaches to a coordinatively grown polymer and this too has been demonstrated.(5) Thus, the scientific basis for the preparation of a 1,4 polybutadiene - isotactic polypropylene block copolymer by such a transformation reaction is well established.

The nature of this transformation reaction is further substaniated by model reactions which have been performed in our laboratory. It was found that the catalyst system of nBuLi/$TiCl_4$ is capable of polymerizing isotactic polypropylene under the same conditions described above. The resultant purified polypropylene has an isotactic index(6) of 90%, a melting point of 160°C and a crystallintiy of 30 to 40%. Similarly, another model reaction was performed in which 1,1 diphenyl ethylene was added to a solution of nBuLi in hexane followed by $TiCl_4$ and butadiene monomer. The extent of reaction was kept low and the resultant trans 1,4 polybutadiene was shown by high resolution NMR to contain the 1,1 diphenyl ethylene endgroup.

Observations made during the block copolymer polymerization may also serve as indications of a novel product. The net recovery of polymer from the transformation reaction was a 33%

increase over the weight of butadiene polymerized. The overall yield of block copolymer material was 15% based on the total weight of polymer recovered. The remaining 85% is polybutadiene which is easily removed by extraction. The overall catalyst efficiency was 825 grams of block material per mole of titanium. Since it was estimated that only 35% of the living polybutadienyl lithium reacted, then the yield of copolymer based on the reacted polybutadiene was 50%.

High temperature gel permeation chromatography provided the first good evidence of block copolymer formation. The chromatogram of a matched polybutadiene/polypropylene blend (3) showed two distinct elutions corresponding to the homopolymer fractions (iPP M = 250,000; Mw/Mn = 5 and PBD M = 15,000; Mw/Mn = 1.8) based upon the elution volumes of polystyrene standards. The chromatogram of the copolymer material exhibits only one, slightly broadened peak (M = 300,000; Mw/Mn = 8-10) at a lower elution volume than that of the isotactic polypropylene made under similar reaction conditions.

Additional information on the difference between the copolymer and the blend was obtained by thermal analysis (DSC and dynamic-mechanical analysis). The DSC showed three distinct transitions for both the blend and the copolymer but at distinctly different temperatures. The blend exhibits two distinct glass transitions at -85 and 0°C (PBD and iPP, respectively) as well as a melting endotherm with a maximum in the range of 150 - 158°C, depending on thermal history. The blend's polypropylene has a crystallinity of about 15%. On the other hand, the copolymer exhibits a broad glass transition (-75 to -55°C) centered about -65°C and a more distinct one at +3°C. The melting behavior of the copolymer is slightly different from that of the blend in that its melting range is 152 - 160°C with about 20% crystallinity. The DSC was also used to study the crystallization behavior of these samples. For the most part the block copolymer crystallizes earlier than the blend either at the same crystallization temperature or at the same cooling rate. Currently, more quantitative work is being done in order to explore more fully this difference in crystallization behavior.

Dynamic-mechanical analysis also resulted in data verifying a significant difference between the blend and the copolymer. The blend exhibits two loss peaks at -93 and -7°C. The room temperature storage modulus of the blend is on the order of 3×10^8 dynes/cm^2 while that of the copolymer is considerably higher, 2×10^9 dynes/cm^2. The copolymer also exhibits two loss peaks but at -75 and -2°C respectively. In general, the loss peak associated with the polybutadiene phase is broader and at a higher temperature in the copolymer than the blend. A comparison of the copolymer and blend moduli curves is given in Figure 1.

The most conclusive evidence for block copolymer formation is that obtained by microscopy, especially TEM. While both optical and scanning electron microscopy show distinct differences between the morphology of the blend and the copolymer, transmission electron microscopy shows clear evidence of microphase separation on the order of 400 A in the case of the copolymer (see Figure 2). This regularity and size is typical of that exhibited by block copolymers.

CONCLUSION

From the nature of the polymerization mechanism, the subsequent fractionation and characterization of the reaction products, and the transmission electron microscopy, we conclude that we have produced a novel block copolymer of 1,4 polybutadiene and isotactic polypropylene. Future work is aimed at a closer study of the copolymer's properties and its effects in blends with polypropylene and/or polybutadiene. From an understanding of the structure-property relationships of block copolymer - homopolymer blends it may be possible to modify polypropylene's properties (eg. impact strength) in ways previously unobtainable.

ACKNOWLEDGEMENTS

This research is supported by the Office of Naval Research.

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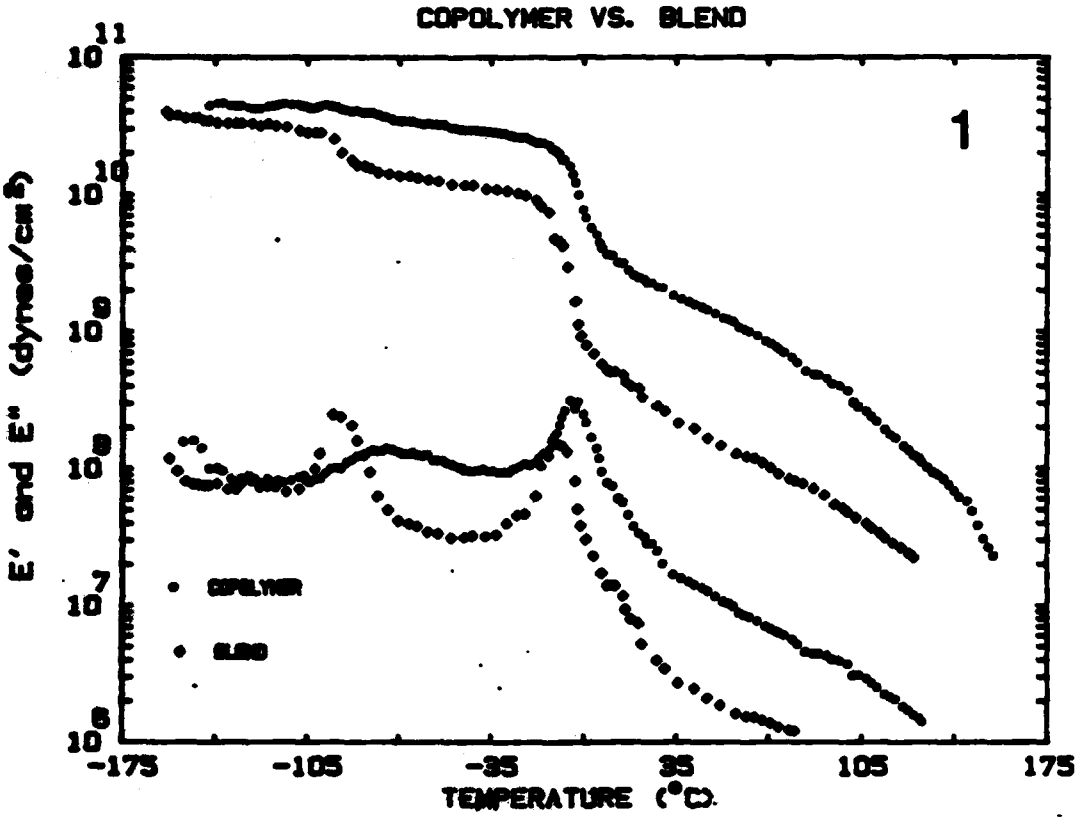
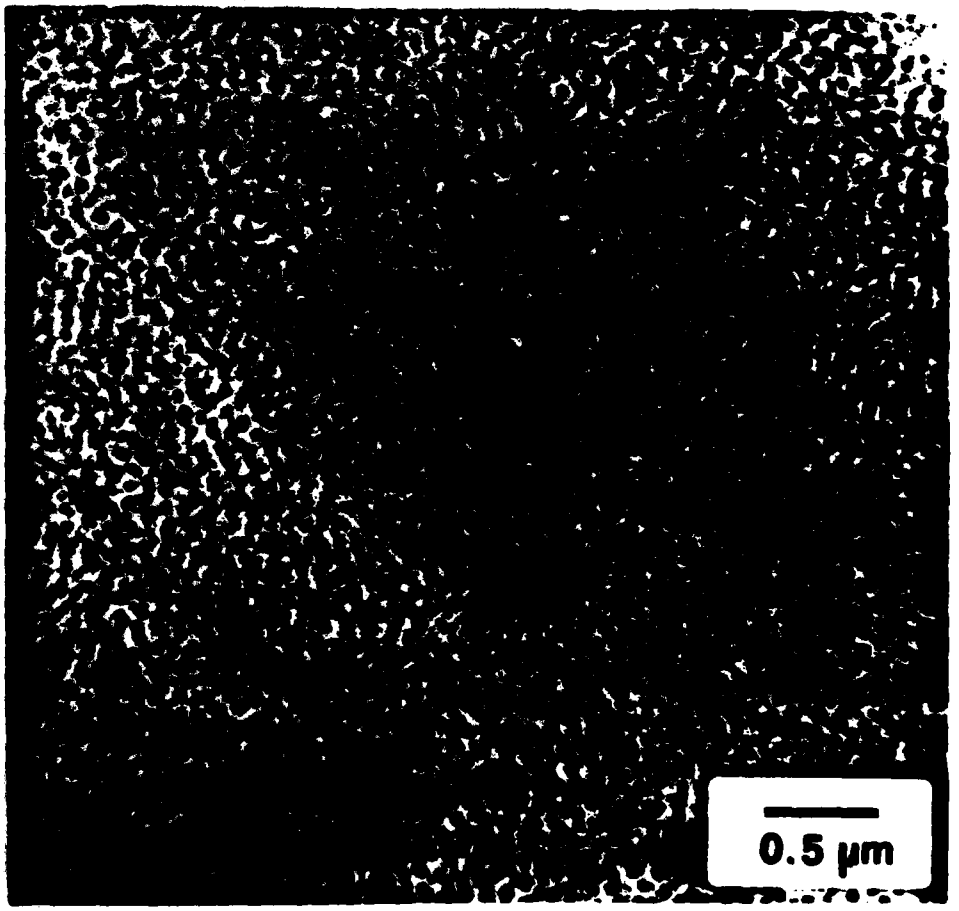
6. Isotactic Index = A_{995}/A_{975} x 100% by IR.

FIGURE CAPTIONS

Figure 1: Dynamic-Mechanical Behavior of Copolymer and Blend Measured at 11 Hz.

Figure 2: Transmission Electron Micrograph of OsO_4 Stained Thin Section of Copolymer.


COPOLYMER VS. BLEND
1
E' and E" (dynes/cm²)
COPOLYMER
BLEND
TEMPERATURE (°C)
-175
-105
-35
35
105
175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