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Macromers by Carbo-Cationic Polymerization

5. Synthesis of Polyisobutenyl–Dicyclopentadiene and Its Terpolymerization with Ethylene-Propylene to a New EPM-Isobutylene Graft

Michael F. Farona* and J. P. Kennedy**

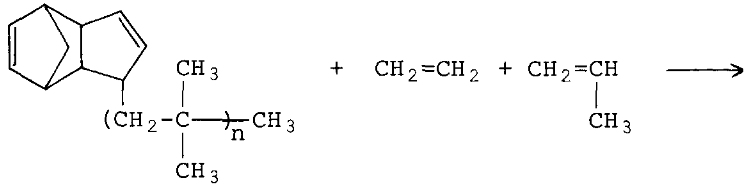
Summary

An EPDM graft terpolymer was prepared using the macromer polyisobutenyldicyclopentadiene (PIB-DCp). Terpolymerization of PIB-DCp with ethylene and propylene led to a new material containing one branch per chain. The terpolymer was characterized by GPC which revealed a single, rather narrow peak in the chromatogram. Osmometric measurements indicated a $\overline{M}n$ of 60,000, and the overall composition of the graft was determined by nmr spectrometry.

Introduction

In the course of our continued investigation on macromers (e.g., previous paper in this series, ref. 1) we have developed a method for the preparation of polyisobutenyldicyclopentadiene (PIB-DCp) (2). The synthesis involves the polymerization of isobutylene by the dicyclopentadienyl chloride inifer in conjunction with $(C_2H_5)_2AlCl$ coinitiator in methyl chloride diluent.

It occurred to us that this novel macromer would be of interest as a new termonomer in the terpolymerization with ethylene-propylene. Since dicyclopentadiene has been shown to terpolymerize readily with ethylene-propylene by the use of soluble Ziegler-Natta type catalysts (3), and ethylene-propylene-dicyclopentadiene terpolymers are commercial commodities (e.g., Royalene® of Uniroyal), the terpolymerization of PIB-DCp was also expected to proceed without undue difficulties. The reaction product of this terpolymerization is a novel graft copolymer consisting of the rubbery ethylene-propylene random copolymer backbone carrying rubbery polyisobutylene branches:



PIB-DCp

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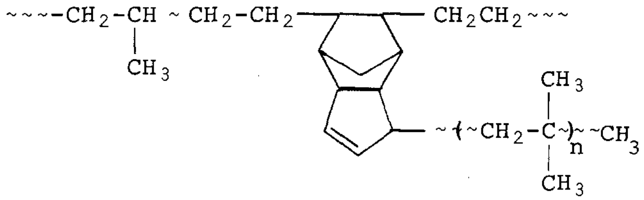
*Department of Chemistry The University of Akron, Akron, Ohio 44325, USA

**Department of Polymer Science The University of Akron, Akron, Ohio 44325, USA



EPDM-g-PIB

The graft would be still vulcanizable (availability of allylic hydrogen), and would exhibit properties combining those of the parent EPDM backbone and the PIB branches.

This preliminary report concerns an outline of the synthesis of the PIB-DCp macromer, a description of the graft terpolymerization of PIB-DCp with ethylene and propylene, and the characterization of the novel graft copolymer EPDM-g-PIB.

Experimental

Solvents and starting materials. n-Heptane was used to dissolve the catalyst components and the macromer, as well as the solvent for the polymerization reaction. It was distilled over $LiAlH_4$, and collected and stored under nitrogen over molecular sieves.

The catalyst system was $VOCl_3$ (Aldrich) and $(C_2H_5)_3Al_2Cl_3$ (Texas Alkyls). n-Heptane solutions of these compounds were made up as follows: $VOCl_3$ = 0.03 M; $(C_2H_5)_3Al_2Cl_3$ = 0.12 M.

Physical methods. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 521 Spectrophotometer. ^{1}H nuclear magnetic resonance (nmr) were obtained with a Varian EM360 spectrometer using CS_2 solutions and TMS as the internal standard. Ultraviolet spectra were taken on an American Instrument Co. DW2A spectrophotometer. Molecular weights were measured by vapor pressure osmometry (Knauer VPO, toluene at 40°C), membrane osmometry (Mechrolab 503 high speed osmometer, toluene solutions at 37°C), and gel permeation chromatography (Waters Associates 6000 A pump, UV and RI detectors, micro-Styragel columns 10^6, 10^5, 10^4, 10^3, 500 Å; elution counts were calibrated by polyisobutylene standards, THF solutions).

Preparation of 1-chlorodicyclopentadiene, DCp-Cl. This compound was synthesized by the chlorination of dicyclopentadiene-1-ol according to Dilling et al. (4). The carbinol was prepared by allylic oxidation of dicyclopentadiene using selenium dioxide according to Woodward and Katz (5).

Preparation of PIB-DCp. The polymerization was carried out at -50°C in a dry box (2). A methyl chloride solution (1 ℓ) containing 0.2 g (1.2 x 10^{-3} mol) DCp-Cl and 164 ml (2 mol) isobutylene was treated with 1 x 10^{-2} mol $(C_2H_5)_2AlCl$. The resulting polymer was purified by adding the charge to methanol, recovering the precipitated polymer, and reprecipitating from n-heptane-methanol. The last traces of solvent were removed in vacuum at ambient temperature, yielding 85 g of polymer. The PIB-DCp was cracked at 160°C under vacuum, which removed cyclopentadiene, leaving polyisobutenylcyclopentadiene PIB-Cp. The amount of DCp head group was determined by comparing ultraviolet spectra of the PIB-Cp against a calibration curve of *n*-propylcyclopentadiene (see below). The $\overline{Mn}$ of the polymer by GPC, was 27,000.

Preparation of *n*-propylcyclopentadiene, PCp. This compound was prepared in a manner analogous to that described by Kraihanzel and Lossee for the synthesis of trimethylsilylcyclopentadiene (6). To a 500 ml three-necked flask equipped with a nitrogen inlet, addition funnel, and a condenser was placed 235 ml THF and 18.8 g (0.818 mol) sodium. Cyclopentadiene (81 ml, 63.8 g, 0.967 mol) was added dropwise, and the reaction mixture was stirred overnight. Then 95.7 g (0.778 mol) *n*-propyl bromide was added dropwise over 2 hr at room temperature, during which time the exothermic reaction raised the temperature of the mixture to the reflux point. The product was added to water and extracted with *n*-hexane. The organic layer was separated and washed several times with water. The *n*-hexane was removed by an aspirator and the crude product was distilled. PCp showed a boiling point of 45°C at 15 mm. The yield was 34 g, 41.6%.

Preparation of ethylene-propylene-polyisobutenyldicyclopentadiene terpolymer EPDM-*g*-PIB. The polymerization was carried out in a 500 ml, four-necked flask which was dried in an oven and then flamed out under nitrogen with a Bunsen burner. Into the flask was placed 200 ml dry *n*-heptane and a magnetic stirrer. Rubber septums were placed on three necks, and to the fourth was attached a pressure-equalized separatory funnel containing 50 ml of a *n*-heptane solution of PIB-DCp at a concentration of 0.09 g/ml. The flask was immersed in a water bath at ambient temperature. Ethylene and propylene were introduced into the *n*-heptane through individual septums from their respective trains. Both gases were passed through CuO catalyst at 150°C to remove any hydrogen, and then through Drierite to remove moisture. The flow rate of each gas was adjusted through flow meters at 1 liter/min. The *n*-heptane solvent was saturated with the two gases (15 min), whereupon the PIB-DCp solution was added dropwise to the reaction mixture over a period of 7 min. Simultaneous with addition of the polymer solution, the catalyst components were added by means of a syringe pump (Sage Instruments Model 351) at a rate of 1 ml per min. In this manner, the Al:V ratio is constant at 4:1. At the end of delivery of the macromer, the addition of catalyst components, ethylene and propylene was terminated. The solution was allowed to stir for 5 min, then poured into 500 ml of methanol containing 5 g of N-phenyl-β-naphthylamine, resulting in the precipitation of the graft terpolymer. The polymer was then collected by filtration and redissolved in *n*-heptane. The *n*-heptane was removed by rotary evaporation; the last traces of solvent were removed in vacuum at 50°C. The yield was 7.5 g. The yield depends on the time of addition of the reactants. When the macromer was added over a period of 12 min, the yield was 14 g.

Results and Discussion

Ethylene propylene diene polymers (EPDM) are of commercial interest; among the more important dienes are dicyclopentadiene, 5-ethylidene-2-norbornene, and 1,4-hexadiene. The object of this research was to prepare an EPDM where the diene was part of a macromer. The macromer selected was PIB-DCp, i.e., a polyisobutylene carrying a dicyclopentadiene head group, and it was synthesized by cationic polymerization of isobutylene initiated by a DCp carbenium ion.

In order to determine the percent of head group in the macromer, *n*-propylcyclopentadiene was synthesized, and calibration curves were made. The PIB-DCp was cracked at 160°C, yielding PIB-Cp, from which standard solutions were prepared. It was calculated that every PIB molecule carried one Cp head group, $\overline{F_m} = 1.0$. The molecular weight ($\bar{M}n$) of PIB-DCp was 27,000 by GPC.

The preparation of the graft polymer was carried out according to published procedures using a continuous addition of catalyst and olefins (7). It was necessary to determine that a graft was prepared, rather than a mixture of ethylene-propylene polymer and PIB-DCp. This was accomplished by GPC, which revealed a single rather narrow, symmetrical peak in the chromatogram. The $\bar{M}n$ of the graft copolymer was 60,000 by osmometry.

According to visual examination a physical blend of about equal parts of EPDM and PIB (prepared by mixing CS_2 solutions of EPDM and PIB and evaporating the solvent) was quite different in appearance from a graft copolymer: while the physical blend was a very tacky semisolid, the EPDM-*g*-PIB was a homogeneous nontacky rubber.

The overall composition of the graft can be estimated from molecular weight measurements and independently by ^1H nmr spectroscopy.

Since the $\bar{M}n$ of the PIB-DCp is 27,000 and that of the EPDM-*g*-PIB is 60,000, the overall composition of the graft copolymer is PIB/EPDM = 45/55.

Similar composition data have been obtained by ^1H nmr spectroscopy. The ^1H nmr spectrum of the EPDM-*g*-PIB shows four clearly resolved resonances (Figure 1): The signals at $\delta = 1.2$ and 0.82 ppm are due to the EPDM backbone, whereas those at $\delta = 1.33$ and 1.04 ppm are characteristic of the PIB branches (assignments were made with authentic EPM and PIB-DCp samples). Integration yields PIB/EPDM = 47/53, in accord with the estimation made by molecular weight comparisons.

According to the above data, the number of PIB branches per EPDM backbone is close to one. This value might seem low in view of the fact that DCp is about 7 times more reactive than propylene (8). However, the great bulk of the attached PIB should lead to rather severe steric compression, which would be reflected in an apparent decrease in activity of the DCp to propylene. We are not prepared at this time to specify the location of the branch, whether terminal or internal with respect to the chain.

In conclusion, the facts presented in this communication clearly show that a novel graft copolymer EPDM-*g*-PIB can be conveniently prepared by terpolymerizing ethylene/propylene with the PIB-DCp macromer under conventional coordinative copolymerization conditions.

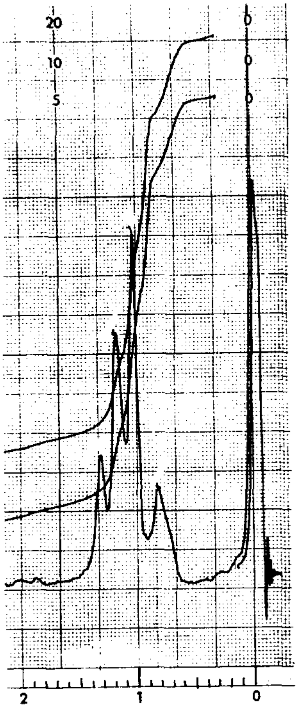


Figure 1
^1H NMR Spectrum of EPDM-g-PIB
Between δ 0-2 PPM.

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