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The Synthesis of an Isobutylene-α-Methylstyrene Block Copolymer with Olefinic Head-Group: $(CH_3)_2C{=}CHCH_2$-PIB-b-PαMeSt*

Joseph P. Kennedy, S. Y. Huang and Robert Alan Smith**

Institute of Polymer Science, University of Akron, Akron, Ohio 44325, USA

Summary

The title head-functionalized block copolymer was synthesized by first preparing a polyisobutylene carrying a $(CH_3)_2C{=}CH_2$- head-group and -Cl end-group, and subsequently starting the block copolymerization of α-methylstyrene from the -Cl terminus.

Introduction

Recent leads (KENNEDY, et al. 1977a,b) concerning controlled initiation and termination of cationic olefin polymerizations have been exploited for the synthesis of functional block copolymers $F\text{-}A_n\text{-}B_n$, where F = olefin function and A_n, B_n are polyolefin blocks such as polyisobutylene PIB, polystyrene PSt and Poly(α-methylstyrene) PαMeSt. This preliminary communication deals specifically with the synthesis and characterization of $(CH_3)_2C{=}CHCH_2$-PIB-b-PαMeSt.

The synthesis of $(CH_3)_2C{=}CH\text{-}CH_2$-PIB-b-PαMeSt is based on combination of three leads previously developed in our laboratories: 1. Controlled initiation of isobutylene polymerization by the $(CH_3)_2C{=}CHCH_2Cl/BCl_3$ initiating system which gives rise to allyl head-groups, 2. Controlled termination (i.e., termination in the absence of chain transfer to monomer) of isobutylene polymerization in the presence of $BCl_4^{\ominus}$ counter-anions which results in $-C(CH_3)_2Cl$ end-groups, and 3. Controlled initiation of olefin polymerization including α-methylstyrene by tertiary chlorines in conjunction with Et_2AlCl. The equations help to visualize the synthesis sequence:

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*7th in the series: Cationic Polymerization with Boron Halides.

**Present address: American Cyanamid Co., Stamford, Conn. 06904

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$$(CH_3)_2C{=}CHCH_2 + BCl_3 \rightleftharpoons (CH_3)_2\overset{\delta\oplus}{C}\cdots CH\cdots\overset{\delta\oplus}{C}H_2 \;\; BCl_4^{\ominus}$$

$$(CH_3)_2\overset{\delta\oplus}{C}\cdots CH\cdots\overset{\delta\oplus}{C}H_2 + n\ \underline{i}\text{-}C_4H_8 \longrightarrow (CH_3)_2C{=}CH\text{-}CH_2\sim\sim\sim \sim\sim\sim CH_2\overset{\oplus}{C}(CH_3)_2$$

$$(CH_3)_2C{=}CH\text{-}CH_2\sim\sim\sim CH_2\overset{\oplus}{C}(CH_3)_2 \;\; BCl_4^{\ominus} \longrightarrow \underset{\text{I}}{(CH_3)_2C{=}CHCH_2\sim\sim\sim PIB\sim\sim\sim CH_2C(CH_3)_2Cl} + BCl_3$$

$$\text{I} + Et_2AlCl + \underset{\text{II}}{(CH_3)_2C{=}CHCH_2\sim\sim PIB\sim\sim CH_2\overset{\oplus}{C}(CH_3)_2 \;\; Et_2AlCl_2^{\ominus}}$$

$$\text{II} + \alpha\text{-MeSt} \longrightarrow (CH_3)_2C{=}CHCH_2\sim\sim PIB\sim\sim \boxed{\sim\sim P\alpha MeSt\sim\sim}$$

Experimental

BCl$_3$ was used as received. 1-Chloro-3-methyl-2-butene was dried with CaH$_2$ and distilled under vacuum. Et$_2$AlCl was refluxed over NaCl and distilled under reduced pressure. Isobutylene was dried by passing the gas over molecular sieves (4Å) and BaO. α-Methylstyrene was dried with CaH$_2$ and distilled under nitrogen atmosphere.

Details of GPC analyses, membrane osmometry, and vapor pressure osmometry will be published later.

The synthesis of $(CH_3)_2C{=}CHCH_2\sim\sim PIB\sim\sim CH_2C(CH_3)_2Cl$ was carried out at -52°C in a dry box under nitrogen atmosphere using "baked out" flasks charged with $\underline{i}$-C_4H_8 (2.0$\underline{M}$) and $(CH_3)_2C{=}CHCH_2Cl$ (3.0×10^{-2}M) in CH$_2$Cl$_2$ solutions. After thermoequilibrium BCl$_3$ (4.0×10^{-2}M) in CH$_2$Cl$_2$ was added to the stirred charges. Reactions were quenched after 30 mins by few ml of prechilled methanol, the precipitated polyisobutylenes were rapidly filtered and washed with CH$_2$Cl$_2$. The yield of I was 23-25% and $\overline{M}_n$ (by VPO) = 14,000-16,000.

A subsequent blocking step was carried out by dissolving I (2.4g) in methylcyclohexane, adding CH$_2$Cl$_2$ (38 vol.% in final charge of 90 ml) and α-MeSt (0.8 M), cooling the stirred charge to -52° and commencing blocking by introducing Et$_2$AlCl (2.2×10^{-3}M) in CH$_2$Cl$_2$ solution. Blocking was terminated after 30 mins with a few ml methanol. Yield was 55%, $\overline{M}_n$ (by osmometry) = 31,000.

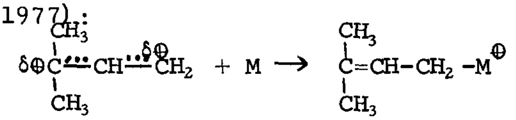
Crude products were purified by selective solvent extraction. First the reaction product was extracted

(Soxhlet) with n-pentane. The n-pentane-insoluble fraction was subsequently extracted by a series of acetone/dioxane mixtures as follows: The n-pentane-insoluble fraction (1g) was stirred in acetone (100 ml), allowed to settle, and an aliquot (10 ml) withdrawn of the supernatant. The amount of polymer and its composition was determined. Then the volume of the withdrawn aliquot was replaced by an equal volume of dioxane (10 ml) and the procedure repeated until the medium consisted predominantly of dioxane. Further details will be given in a subsequent publication.

Results and Discussion

Isobutylene polymerization coinitiated by BCl_3 proceeds in the absence of chain transfer to monomer and with termination by the $BCl_4^{\ominus}$ counter-anion (KENNEDY et al. 1977a,b). Orienting experiments showed that $(CH_3)_2C{=}CHCH_2Cl$ in conjunction with BCl_3 initiates the polymerization of isobutylene at or below -50^0. The presence <u>and</u> position of olefinic unsaturation in PIB prepolymer was proven by two sets of experiments. First the PIB prepolymer obtained with the $(CH_3)_2C{=}CHCH_2Cl/BCl_3/\underline{i}\text{-}C_4H_8$ system was analyzed for unsaturation by epoxidation/titration (DREYFUSS and KENNEDY 1975). Results of these analyses indicated 0.8 -1.3 unsaturation per mole of PIB (details to be published later). Second, the prepolymer was oxidatively degraded by aggressive periodation (KENNEDY and METZLER 1977) and the $\bar{M}_n$ of surviving fragments determined. The $\bar{M}_n$ of the prepolymer did not noticeably change upon this treatment which indicates terminal unsaturation.

Initiation of isobutylene polymerization by the allyl cation $(CH_3)_2\overset{\delta\oplus}{C}\cdots CH\cdots\overset{\delta\oplus}{C}H_2$ may occur at the tertiary or primary carbenium center. According to appropriate model experiments initiation is kinetically controlled and proceeds predominantly from the primary site (KENNEDY et al. 1977):



$$\delta\oplus\underset{CH_3}{\overset{CH_3}{C}}\cdots CH\cdots\overset{\delta\oplus}{C}H_2 + M \longrightarrow \underset{CH_3}{\overset{CH_3}{C}}{=}CH\text{-}CH_2\text{-}M^{\oplus}$$

On the basis of background information and the above experiments we are confident that our PIB prepolymer contains a $(CH_3)_2C{=}CHCH_2\text{-}$ head-group and a tertiary chlorine end-group. Proof positive that the terminal group is in fact a tertiary chlorine was obtained by initiating the polymerization of α-MeSt by the prepolymer using Et_2AlCl coinitiator. Moreover, preliminary experiments showed that αMeSt polymerization initiated by t-BuCl/Et_2AlCl at -30^0 occurs essentially in the absence of chain transfer to monomer (the $1/\overline{DP}_n$ versus 1/M plot exhibits negligible intercept). Thus blocking of αMeSt from the $(CH_3)_2C{=}CH-CH_2$-PIB-Cl prepolymer in conjunction with Et_2AlCl at -50^0 is expected to proceed in the absence of chain transfer to monomer.

Our proposition that the $(CH_3)_2C{=}CHCH_2$-PIB-Cl prepolymer initiates blocking of αMeSt and produces $(CH_3)_2C{=}CHCH_2$-PIB-b-PαMeSt in the absence of chain transfer to monomer is corroborated by molecular weight and composition analyses. For example, a prepolymer with $\overline{M}_n = 14{,}000$ was used to initiate the blocking of αMeSt and after selective extraction the $\overline{M}_n$ and composition of the end product was determined: $\overline{M}_n = 31{,}000$, PIB/PαMeSt (wt.% by NMR) = 48/52. If all the PIB is incorporated into the diblock copolymer and if no PαMeSt is present

$$\overline{M}_n \text{ diblock} = \frac{\overline{M}_n \text{ prepolymer}}{\text{Fraction prepolymer in diblock}}$$

or 14,000/0.48 = 29,200. The agreement between the calculated (29,200) and experimental value (31,000) is quite good which indicates very little homopolymer contamination of either component in the diblock copolymer.

Further, GPC analyses of prepolymers and diblocks showed smooth monomodal distributions. If homopolymer of either component were present, a multimodal MWD or shoulder would appear in the UV or RI traces of the GPC analyses,

Table I shows representative data. A detailed account of the synthesis and characterization of $(CH_3)_2{=}CHCH_2$-PIB-b-Block where Block = PSt and PαMeSt will be published.

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TABLE I

Synthesis of $(CH_3)_2C{=}CHCH_2$-PIB-*b*-PαMeSt*

Step 1. Synthesis of $(CH_3)_2C{=}CHCH_2$-PIB-Cl prepolymer

Expt.	i-C_4H_8/	$(CH_3)_2C{=}CHCH_2$/	BCl_3	Conv.	$\overline{M}_n$
	M	M x 10^2	M x 10^2	%	x10^3
1	2.0	3.0	4.0	25	16
2	2.0	3.0	4.0	23	14

Step 2. Blocking αMeSt from prepolymer obtained in Step 1.

Expt.	αMeSt M	Prepoly- mer, g	Et_2AlCl M x 10^3	Vol. ml	Conv. %	$\overline{M}_n$ x10^3	$\frac{PIB}{PαMeSt}$ %
1a	0.85	3.2	7.0	285	62	47	13/87
2a	0.81	2.4	2.2	90	55	31	48/52

*Both Steps 1 and 2 at -52°C; Solvent systems: Step 1. pure CH_2Cl_2, Step 2. 40/60 CH_2Cl_2/Me-cyclohexane

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