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Ultrahigh Molecular Weight Copolymers of Isobutene and 2,3-Dimethyl-1,3-butadiene Formed Using a Novel Protic Carbocationic Initiator, the 1:2 Adduct of *n*-Octadecanoic (Stearic) Acid and $B(C_6F_5)_3$

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ABSTRACT: Ultrahigh molecular weight copolymers of isobutene (IB) and 2,3-dimethyl-1,3-butadiene (DMBD), analogous to commercial IB−isoprene copolymers, are prepared employing as carbocationic polymerization initiator the highly acidic 1:2 adduct of *n*-octadecanoic (stearic) acid with the electrophilic borane $B(C_6F_5)_3$, $[n\text{-}C_{17}H_{35}CO_2H][B(C_6F_5)_3]_2$. High conversions to gel-free, low-polydispersity materials with weight-average molecular weights well in excess of 3×10^6 are readily obtained, demonstrating the effectiveness of $\{n\text{-}C_{17}H_{35}CO_2[B(C_6F_5)_3]_2\}^-$ as a weakly coordinating anion. Complete ^1H and $^{13}C\{^1H\}$ NMR assignments for the IB−DMBD copolymers, in which the 1,3-diene is incorporated in a 1,4-trans manner, are presented for the first time.

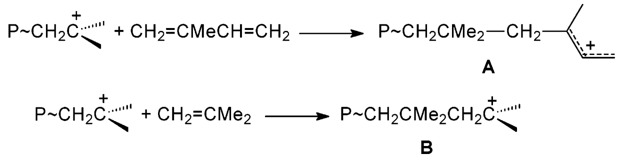
A very important commercial application of isobutene (IB) polymerization is the manufacture of butyl rubber, an IB−isoprene copolymer containing 1−2 mol % isoprene (IP).[1−3] This class of materials is produced commercially via a carbocationic process employing an $AlCl_3$/water mixture in methyl chloride as a protic initiator system. Small amounts of IP (∼1−2.5%) are incorporated into the polymer and result in the formation of a random copolymer that contains IP incorporated predominantly in a 1,4-trans manner.[1−4]

To obtain high molecular weights ($M_w \geq 5 \times 10^5$), cryogenic temperatures (−100 °C) are necessary to minimize the effects of chain transfer processes.[1−4] Indeed, for a given set of conditions, IB−IP copolymers normally display lower average molecular weights than IB homopolymers, and the average molecular weights decrease as the proportion of incorporated IP increases.[1−5] This is because the allylic cation group formed on the incorporation of a molecule of IP (**A** of Scheme 1) is more readily deprotonated by IB monomer than is the tertiary cation formed following incorporation of a molecule of IB (**B** of Scheme 1).

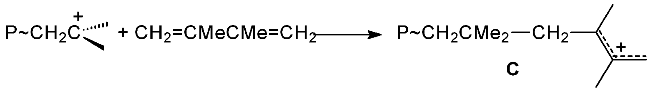
It occurred to us that the use of 2,3-dimethyl-1,3-butadiene (DMBD) in lieu of IP should result in the formation of higher average molecular weight copolymers because the inductive effect of the second methyl group in the resulting allylic cation (**C** of Scheme 2) should render the allylic group less acidic and therefore less prone to undergo deprotonation.

If so, higher molecular weights at lower temperatures should be attainable with DMBD than with IP, and the resulting copolymers could have significant commercial interest. However, aside from older patents,[7,8] there is surprisingly little information in the literature about IB−DMBD copolymers. Cesca et al. have reported the copolymerization of IB and DMBD using $EtAlCl_2$ in 1:1 pentane−CH_2Cl_2 at −70 °C.[9,10] It was anticipated that the presence of the methyl groups would exert a positive influence on the polymerization process, but in fact only low molecular weight ($M_n < 10^4$) copolymers were obtained.

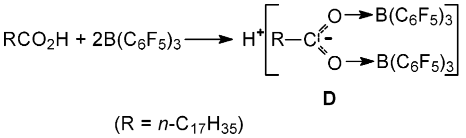
Scheme 1



Scheme 2



Scheme 3



We have recently demonstrated that the 2:1 adduct of $B(C_6F_5)_3$ and *n*-octadecanoic (stearic) acid behaves as a strong acid and reacts with Cp^*TiMe_3 to form an excellent initiator, $[Cp^*TiMe_2]^+$, for the polymerization of IB and the copolymerization of IB with IP.[11] Indeed, the 2:1 adduct is a very good protic initiator in its own right as the counteranion, $\{[n\text{-}C_{17}H_{35}CO_2][B(C_6F_5)_3]_2\}^-$ (as in **D** of Scheme 3) and is very weakly coordinating. and thus high molecular weight polymers and copolymers are readily obtained.[12] The importance of carrying out carbocationic polymerizations in the presence of very weakly coordinating anions, if chain transfer is to be minimized, has been well established.[5,6]

We have now extended our studies to the possibility of synthesizing high molecular weight IB−DMBD copolymers, and this paper describes the successful synthesis of copolymers with weight-average molecular weights well in excess of 3 million.

Experimental Section

NMR spectra were recorded on a Bruker Avance 600 NMR spectrometer. Representative ^1H and $^{13}C\{^1H\}$ NMR spectra are shown in Figures 1 and 2, respectively, and the labeling schemes are shown in Figure 3. For 2D ROESY experiments,

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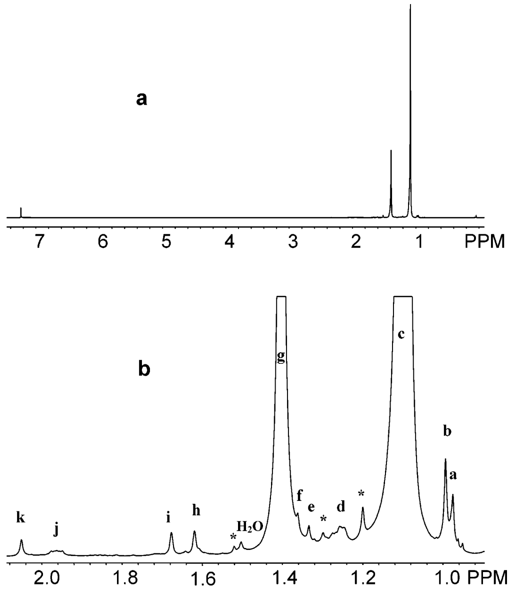

Figure 1. ^{1}H NMR spectrum of (a) a representative isobutylene/2,3-dimethyl-1,3-butadiene copolymer and (b) the spectrum of (a) expanded in the region δ 0.5−2.5. The asterisks indicate the positions of ^{13}C satellites. Refer to Figure 3 for labeling scheme.

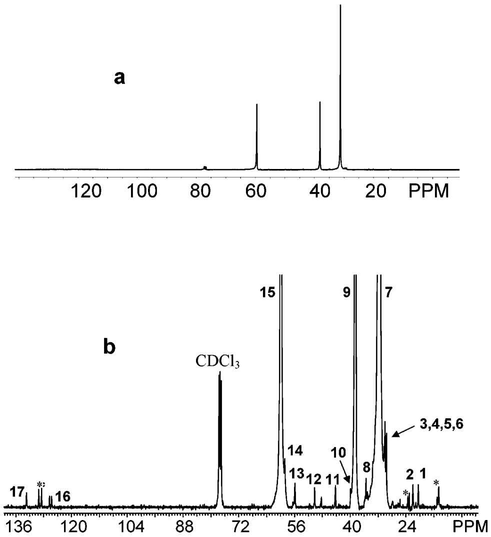

Figure 2. ^{13}C{^{1}H} NMR spectrum of (a) a representative isobutylene/2,3-dimethyl-1,3-butadiene copolymer and (b) the spectrum of (a) expanded. The asterisks indicate resonances of solvent or impurities. Refer to Figure 3 for labeling scheme.

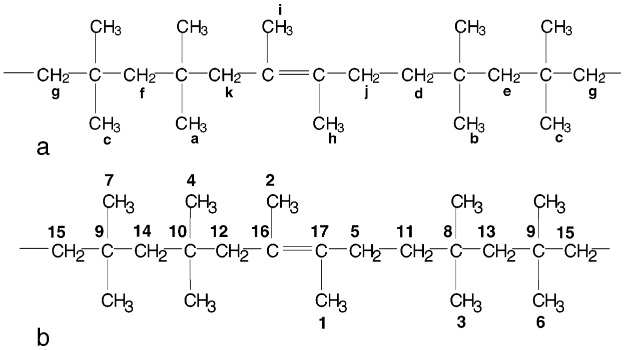

Figure 3. Labeling schemes for (a) the ^{1}H NMR spectra and (b) the ^{13}C{^{1}H} NMR spectra.

we used a spectral window of 3 ppm to gain high digital resolution, a relaxation delay of 1.5−2 s, and a mixing period of 0.3 s. We acquired 2K data points in the detection domain and performed 256 increments in the evolution domain, which was zero-filled to provide a 2K by 2K matrix. Molecular weights were determined on a Waters Associates model GPC-2690 liquid chromatograph equipped with a Waters 2410 RI detector and a series of Styragel HR 5, HR 4E, and HMW 7 separation columns. Calibration of the instrument was done using polystyrene standards calibrated for molecular weights ranging from 770 to 6 500 000 g/mol. The GPC analyses were done using toluene as eluant, with a column temperature of 75 °C and with a solvent flow rate of 1.0 mL/min. All syntheses and initiator manipulations were carried out under dry nitrogen or argon atmospheres using standard Schlenk line techniques or an MBraun Labmaster glovebox. Toluene and methylene chloride were dried by refluxing under nitrogen over sodium metal and calcium hydride, respectively, and were degassed by freeze−pump−thaw procedures prior to use. Nitrogen was purified by passage through a heated column of BASF catalyst followed by a column of dry, activated 3A or 4A molecular sieves (Linde). Isobutene (Air Products or Bayer, purity grade, 99.5%) was purified by passage through columns of 3A molecular sieves and was condensed into a graduated flask which was attached to the reactor. Methyl chloride (Matheson) was also purified by passage through columns of 3A molecular sieves and was condensed directly into the reactor system as described below. The DMBD and *n*-octadecanoic acid were purchased from Aldrich. The DMBD was purified by distillation under reduced pressure and was stored under molecular sieves, while the *n*-octadecanoic acid was purified by recrystallization from hexanes; the purities of both were confirmed by ^{1}H NMR spectroscopy. The compound $B(C_6F_5)_3$[13,14] was synthesized as in the literature and assessed for purity by ^{19}F NMR spectroscopy.

Polymerizations were carried out using a 50 mL glass reactor equipped with a coldfinger condenser (dry ice/2-propanol) and a 12 mL graduated flask which was attached by a sidearm via a ground glass joint, as described previously.[15] The results of the polymerization runs are shown in Table 1; most of the data are averages of 2−4 separate runs. In a typical experiment, a mixture of ~10 mL of IB (~0.11 mol) and ~0.13 g of DMBD (~1.6 mmol) was transferred to the 12 mL graduated flask and frozen in liquid nitrogen (−196 °C), and 13 mL of methyl chloride was transferred to the 50 mL glass reactor, which was also frozen in liquid nitrogen; the entire system was evacuated to ~10^{-3} Torr. The flask was then isolated from the reactor, which was filled with nitrogen, and a freshly prepared solution of n-$C_{17}H_{35}CO_2H$ and $B(C_6F_5)_3$ (1:2 molar ratio; see Table 1 for amounts) in 2 mL of methylene chloride or toluene was also added to the reactor and frozen. The pressure in the reactor was again reduced to ~10^{-3} Torr, the reactor was then positioned in a bath thermostated at a temperature in the range −30 to −85 °C, and the reaction mixture was melted, stirred, and allowed to equilibrate. The contents of the graduated flask were then melted and transferred to the reactor by inverting the flask. Polymerizations proceeded at the vapor pressures of the liquid mixtures (~260 and ~26 Torr for MeCl at −30 and −85 °C, respectively[16]), and in part, because of the exothermicities of the polymerization reactions, the reaction mixtures refluxed vigorously. However, as the refluxing both resulted in good mixing of the reaction mixtures and involved condensation at −78 °C, liquid returning to the reaction mixture following vapor condensation offset the heat of reaction, and the temperatures of the reaction mixtures were generally within ±2 °C of the bath temperatures listed in Table 1.

Polymerizations were terminated after 1 h by pouring the reaction mixtures into 1 L of methanol, after which the resulting polymeric materials were collected and dried. To ensure homogeneity, each sample was dissolved in 50−100 mL of hexanes, the solutions were filtered if necessary, and the pure products were obtained by removing the solvent under reduced pressure. The resulting white, elastic polymers were characterized by GPC and by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy; ^{1}H and ^{13}C{^{1}H} NMR chemical shift data are given in Table 2. In all cases, the wt % of the DMBD incorporated in the copolymers was in the range 0.8−1.3%.

Table 1. Isobutene and 2,3-Dimethyl-1,3-butadiene Copolymerization Using the $B(C_6F_5)_3$/*n*-Octadecanoic Acid System

expt no.	wt of *n*-octadecanoic acid (mg, mM)	wt of $B(C_6F_5)_3$ (mg, mM)	solvent system	temp (°C)	conv (% IB)	% DMBD incorporation	$M_w \times 10^{-6}$	M_w/M_n
1	9, 1.3	32, 2.5	MeCl/toluene	−30	2	1.0	0.33	1.5
2	9, 1.3	32, 2.5	MeCl/toluene	−78	6	0.7	3.2	2.2
3	13, 1.8	48, 3.6	MeCl/toluene	−78	48	0.8	3.3	2.0
4	15, 2.2	57, 4.4	MeCl/toluene	−78	57	1.0	4.3	2.2
5	18, 2.5	64, 5.0	MeCl/toluene	−78	75	1.0	3.8	1.8
6	27, 3.8	96, 7.5	MeCl/toluene	−78	76	0.8	3.1	1.6
7	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−30	87	1.3	0.30	1.5
8	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−40	98	1.3	0.29	1.4
9	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−50	100	1.3	0.44	1.5
10	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−55	100	1.3	0.61	1.5
11	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−60	100	1.3	0.69	1.5
12	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−65	99	1.3	1.6	1.9
13	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−78	78	0.9	4.9	1.8
14	18, 2.5	64, 5.0	$MeCl/CH_2Cl_2$	−85	69	0.9	5.0	1.7

Table 2. ^1H and $^{13}C\{^1H\}$ NMR Data for IB−DMBD Copolymer Containing ∼1 % DMBD, with Comparisons of Literature Data for a Material Containing ∼30% DMBD

peak	obsd	lit.	peak	obsd	lit.[3]
a	0.98	0.9−1.1	**1**	19.9	
b	1.00	0.9−1.1	**2**	21.4	
c	1.08	0.9−1.1	**3**	29.1	
d	1.26	1.1−1.4	**4**	29.4	20.19
e	1.34	1.1−1.4	**5**	29.8	29.58
f	1.37	1.1−1.4	**6**	30.9	31.27
g	1.39	1.1−1.4	**7**	31.3	31.27
h	1.63	1.60	**8**	35.0	35.07
i	1.68	1.60	**9**	38.0	38.16
j	1.97	1.98	**10**	38.5	
k	2.05	1.98	**11**	43.7	43.9
			12	49.7	49.84
			13	55.4	55.5
			14	58.3	58.42
			15	59.5	59.56
			16	126.0	125.9−126.0
			17	132.6	132.4−132.7

Results and Discussion

To obtain PIB and IB−IP copolymers of high molecular weight, it is normally essential to carry out the polymerization at cryogenic temperatures where the rates of chain transfer reactions are reduced.[1−6] However, cationic polymerizations exhibit high propagation rates even at low temperatures, and the corresponding heat released may be difficult to control unless the viscosity of the reaction mixtures is kept low and the solution is extremely well mixed. Similar problems were anticipated here, and to minimize the effects of heating, all of the copolymerization experiments were carried out in a reactor immersed in a cold bath and with the reaction mixture maintained under reduced pressure such that the accompanying refluxing served both to maximize mixing and to remove much of the heat of reaction.[15]

Given our earlier success using the 2:1 adduct of the borane, $B(C_6F_5)_3$, with the long chain *n*-octadecanoic acid,[11,12] we utilized in this study the same 2:1 adduct, $[n\text{-}C_{17}H_{35}CO_2H][B(C_6F_5)_3]_2$, used previously (**D** of Scheme 3). This behaves as an excellent protic initiator for IB polymerization and IB−IP copolymerization, and as shown in Table 1, it also behaves as an excellent initiator for IB−DMBD copolymerization.

The polymerization experiments were carried out using ∼10 mL of IB in 15 mL of either of methyl chloride−toluene or methyl chloride−methylene chloride, over a range of temperatures (controlled to within ±2 °C) and with varying amounts of initiator. In all cases the amount of DMBD in the feedstock was ∼2 wt %. Molecular weight data for the products formed are given in Table 1; in all cases near unimodal distributions were observed in the GPC plots. IB conversions were quite low in methyl chloride−toluene when the amount of initiator was at a minimum (experiments 1, 2), probably because of the effects of trace contaminants as conversions increased as the amount of initiator increased (experiments 3−6). On the other hand, IB conversions were consistently high in the more polar solvent mix, methyl chloride−methylene chloride. Similar results have been obtained in IB−IP copolymerizations.[11,12]

Changing the temperature had little obvious effect on the conversions or the molecular weight distributions, both being in the ranges observed previously for IB−IP copolymerizations.[11] However, if the concentration of initiator were kept constant, the temperature had a major influence on molecular weights (experiments 7−14). The values of M_w obtained in methyl chloride−methylene chloride increase from 0.3×10^6 to 5.0×10^6 on going from −30 to −85 °C, while all of the materials obtained in methyl chloride−toluene at −78 °C have weight-average molecular weights in excess of 3×10^6. These molecular weights are quite notable, as they are significantly higher than has been previously observed for IB−IP copolymerizations by conventional initiators[1−3] or, for that matter, by protic initiators in the presence of very weakly coordinating anions.[5,6] Thus, our hypothesis, rationalized above, that higher molecular weights might be obtained using DMBD seems to have been substantiated.

We show in Figures 1 and 2 representative ^1H and $^{13}C\{^1H\}$ NMR spectra. The structures, with atom labels, are shown in parts a and b of Figure 3, respectively, and the chemical shifts and assignments are shown in Table 2 where they are compared with literature data.[9,10] As can be seen, the degree of agreement with the literature assignments is generally only fair. However, while the previous data were obtained at 100 MHz for ^1H and 25 MHz for ^{13}C,[9,10] those reported here were obtained at 600 and 125 MHz, respectively, and thus have the advantage of much greater chemical shift dispersion. In addition, the assignments made here have also been confirmed by 2D HMBC, COSY, and HSQC studies, techniques not available at the time of the earlier work.

As can be seen from Figures 1 and 2, the methyl and methylene resonances of the IB backbone are prominent in the ^1H spectrum at δ 1.08 and 1.39, respectively, while the analogous IB backbone methyl, methylene, and quaternary resonances are observed in the $^{13}C\{^1H\}$

spectrum at δ 31.30, 59.50, and 38.00, respectively. There are no resonances assignable to vinyl hydrogens in the ^{1}H NMR spectrum in the region δ 4.5−5.5, indicating that 1,2-incorporation does not occur. However, as shown in the expanded spectra, there are many very weak resonances, labeled **a**−**k** in the ^{1}H spectrum and **1**−**17** in the ^{13}C{^{1}H} spectrum, which are to be assigned to DMBD, IB−DMBD, and DMBD−IB units. It was on the basis of comparison of the relative intensity of the DMBD resonance at δ 2.05 with that of the main chain IB resonance at δ 1.08 that we deduced the degrees of incorporation of the diene into the copolymers.

Although previous workers were able to show that incorporation of DMBD into a copolymer with IB was highly stereoselective, i.e., either 1,4-cis or 1,4-trans, they could only assume a trans incorporation because that had been demonstrated for other 1,3-dienes.[9,10] We therefore carried out a 2D ROESY experiment on a representative sample, observing cross-peaks between the methylene resonance of site **k** of Table 2 and Figure 3a with those of the methyl resonances of sites **i** and **h** but not with that the methylene resonance of site **j**. Therefore, the methylene groups **k** and **j** are relatively well separated in space, and the DMBD is indeed incorporated in 1,4-trans fashion.

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