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Copolymerization of Isobutene with 4-(2-Hydroxyl-2-methylpropyl) Styrene Co-initiated by TiCl_4 in the Presence of ED

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ABSTRACT

The carbocationic copolymerization of isobutene with an inimer (initiator-monomer), namely 4-(2-hydroxyl-2-methylpropyl)styrene, in the presence of TiCl_4 as a co-initiator and external electron donors (EDs) in hexane and methane chloride mixture at -80°C were investigated. The GPC traces recorded by UV detector and the $^1\text{H-NMR}$ spectra of the copolymers demonstrated that the 4-(2-hydroxyl-2-methylpropyl)styrene could copolymerize with isobutene and homopolymerize carbocationically. The molecular weights of the polymers obtained by using 4-(2-hydroxyl-2-methylpropyl)styrene as an inimer are obviously higher than that of using 2-benzenyl-propan-2-ol as an initiator when all the other reaction conditions were kept the same. The molecular weight increased almost linearly with the evolution of the monomer conversion at the lower conversion and increased drastically at the higher conversion. The curve of the \bar{M} vs. conversion somewhat resemble the polycondensation.

Key Words: Isobutene; 4-(2-Hydroxyl-2-methylpropyl)styrene; Cationic copolymerization; Branched polymer; Electron donor.

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INTRODUCTION

Branched polymers are of substantial commercial interest due to markedly lower viscosity and less shear sensitivity than their linear counterparts.^[1] Among all the existing branched polymers, dendrimers appear to be the most interesting because of their spherical symmetry structure.^[2,3] Conventionally, hyperbranched polymers have been prepared by polycondensation reactions of AB₂ monomers.^[4] However, the often complicated and time-consuming synthetic routes associated with this class of branched polymers present a major drawback in commercial application.

A novel approach was introduced in the early 1990s by Frechet et al.,^[5] termed “self-condensing vinyl polymerization” (SCVP), allowing the synthesis of hyperbranched polymers using vinyl monomers having the general structure AB*, where A stands for a double bond and B* represents an initiating group. These molecules combine the roles of an initiator and a monomer and therefore, have been called “inimer”.^[6,7] This approach has been applied to various types of living polymerizations, i.e., cationic,^[5] ATRP,^[8,9] nitroxide-mediated radical polymerizations,^[10] GTP,^[11,12] and even ring-opening polymerization.^[13]

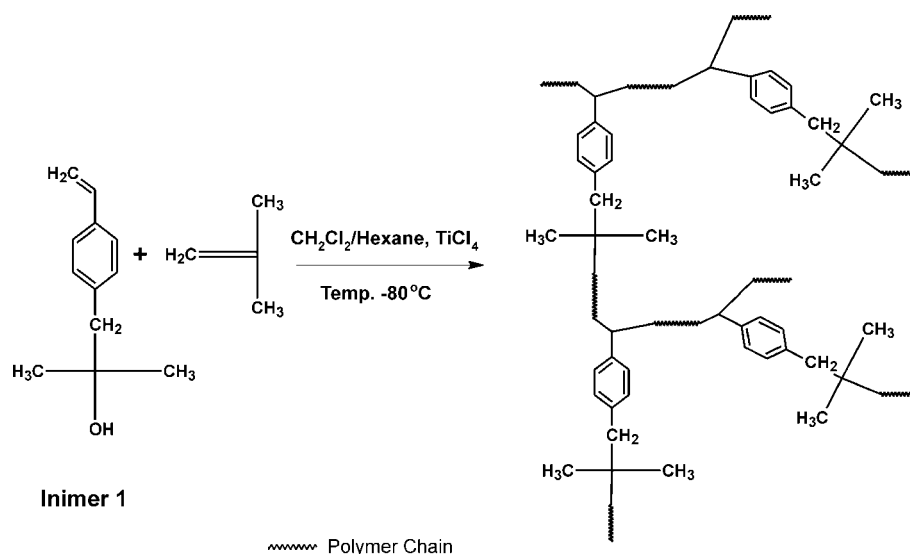
Alternatively, a commercially feasible route for the synthesis of highly branched polymers called “self-condensing vinyl copolymerization (SCVCP)” was recently introduced.^[7] In this method, a small amount of suitable inimer is copolymerized with conventional monomers leading to highly branched polymers. Although the degree of branching of the SCVCP copolymers is lower than that of SCVP homopolymers, the solution properties such as intrinsic viscosity and radius of gyration should be less than proportional, because branched polymers, above a limiting molecular weight, are self-similar objects.^[14] Therefore, a copolymerization is an economic approach to obtain highly branched polymers, especially when aiming at controlling rheology.

To our knowledge, the highly branched polyisobutene was first proposed by Nuyken et al.^[15] in an attempt to synthesize macromonomers by cationic copolymerization of isobutene with p-chloromethyl styrene. Puskas et al.^[7] successfully synthesized hyperbranched PIB by SCVCP method using 4-(2-hydroxyisopropyl) styrene as inimer in a “one-pot” process by living cationic initiation system. Recently, the effect of reaction conditions on the synthesis of hyperbranched polyisobutene using 4-(2-methoxyisopropyl) styrene was investigated.^[16] It was shown that the branching frequencies determined by the selective destruction remain in agreement with calculated values.

This paper describes the results of the SCVCP of the inimer 4-(2-hydroxy-2-methylpropyl) styrene (**Inimer 1**) with isobutene (Sch. 1 is the proposed mechanism for preparation of highly branched polyisobutene). The designing of **Inimer 1** as inimer is based on the following viewpoints: (1) the structure of the initiating species formed by the **Inimer 1** is very similar with propagation chain species, i.e., the ratio of the isobutene addition to the initiating species is almost equal to the ratio of the chain propagation, and this is expected to be favorable to produce the hyperbranched polyisobutene in a much controlled manner; and (2) **Inimer 1** could be easily prepared from commercial available p-chloromethyl styrene than others.

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Scheme 1. Preparation of hyperbranched PIBs.

EXPERIMENTAL

Materials

CH_2Cl_2 (Beijing Yili Fine Chemical Company, AR) and n-Hexane (Beijing Chemical Factory, AR) was refluxed over CaH_2 for 24 hrs, and then distilled before use. TiCl_4 (Beijing Chaoyang Xihui Chemical Factory, AR), p-chloromethylstyrene (ARCOS), 2,6-ditertbutyl pyridine (DtBP, Aldrich) and 2,6-dimethyl pyridine (DMP, Aldrich) and benzyl chloride (Beijing Chemical Factory) are used as received. Isobutene (Yanshan PetroChem Company) was used without further purification. Pyridine (AR, Beijing Chemical Factory) was dried over KOH and distilled before use.

Synthesis of 4-(2-Hydroxyl-2-methylpropyl) Styrene and 2-Benzenyl-propan-2-ol

4-(2-hydroxyl-2-methylpropyl) styrene was synthesized by the reaction of p-chloromethyl styrene (0.07 mol) and acetone (0.075 mol) with crushed magnesium (2.1 g, 0.0875 mol), heated in a dry flask under N_2 , purged for 30 min and allowed to cool in total 200 ml ether using a procedure which minimizes Wurtz coupling.^[17] The solution was poured onto saturated aqueous NH_4Cl (30 ml) and ice. The organic layer was separated and the aqueous layer washed with ether twice. The combined organic layers were washed with water twice and brine, dried over MgSO_4 , filtered and evaporated to dryness. The amount of crude product recovered was 8.812 g (70.5% mol). Then, the crude product was purified by elution through a short plug of silica with CH_2CH_2 to give pure 4-(2-hydroxyl-2-methylpropyl)styrene 6.690 g (53.5% mol). $^1\text{H-NMR}$ (CD_3Cl with D_2O) δ 1.21

(s,6H,—CH₃), δ 1.44 (s,1H,—OH), δ 2.74 (s,2H,—CH₂—), δ 5.22–5.74 (dd,2H,CH₂=), δ 6.64–6.74 (q,1H,=CH—), δ 7.14–7.36 (m, 4H, aromatic). 2-Benzenyl-propan-2-ol was prepared by the similar procedure as 4-(2-hydroxyl-2-methylpropyl) styrene. The crude product was distilled (bp 74–76°C, 9 mmHg). ¹H-NMR (CD₃Cl with D₂O) δ 1.21 (s,6H,—CH₃), δ 1.88 (s,1H,—OH), δ 2.74 (s,2H,—CH₂—), δ 7.18–7.31 (m, 5H, aromatic).

Polymerizations

The polymerizations were carried out in tube-like glass reactors. The reactors were first purged with dry nitrogen, then evacuated and flamed up simultaneously. The operation was repeated three times. The solvents, initiator, and inimer solution were transferred by syringes into the reactors. Then, these mixtures were cooled by ethanol/liquid nitrogen bath to –80°C before IB was added. Polymerizations were started by adding a predetermined amount of TiCl₄ with a syringe. Prechilled methanol was used for quenching the polymerization. The polymer products were purified repeatedly by dissolution (petroleum ether) and/precipitation (methanol). The conversions were determined gravimetrically.

Bond Destruction by the Selective Oxidative Degradation

Kennedy et al.^[18] reported the selective oxidative degradation of the three-arm star-branched PIB having aromatic core. This method was adapted to determine the branching number of hyperbranched PIB by Puskas et al.^[7,16]

Characterizations

¹H-NMR spectra (in CDCl₃) were recorded by a VXR 300S spectrometer at room temperature. Molecular weights were determined by GPC (Waters) equipped a series Styragel columns (HT3, HT5 and HT6E), a RI detector (Waters 2410) and a UV detector (Waters 996, Photodiode Array Detector).

RESULTS AND DISCUSSION

Copolymerization of Isobutene with 4-(2-Hydroxyl-2-methylpropyl) Styrene in the Presence of Various Electron Donors and/or Proton Trap

It has been found that living carbocationic polymerization of olefins can be achieved by using various initiators in conjunction with Lewis acids (co-initiator) and in the presence of a wide variety of externally electron donors or a proton trap (DtBP).^[19] The copolymerization of isobutene with **Inimer 1** in the presence and absence of external additives was carried out with TiCl₄ as co-initiator in mixed solvents of CH₂Cl₂ and n-C₆H₁₄. The results are summarized in Table 1. Figure 1 displays the GPC traces recorded

Table 1. The copolymerization of isobutene with **Inimer 1**.^a

Sample ID	Additive	Yield, % ^b	\bar{M}_n	\bar{M}_w/\bar{M}_n
HV-1 ^c	No	93.4	44300	3.71
HV-3	No	87.2	19100	2.26
HV-6	DtBP	94.7	8340	1.55
HV-7	Pyridine	90.3	24100	1.53
HV-8	DMP	88.7	15600	1.68

^a $[\text{IB}]_0 = 1.29 \text{ M}$, $[\text{INIMER}]_0 = 0.0194 \text{ M}$, $[\text{TiCl}_4] = 0.0387 \text{ M}$, $[\text{Additive}] = 0.0129 \text{ M}$, Solvent: 15 ml CH_2Cl_2 + 10 ml $n\text{-C}_6\text{H}_{14}$, Reaction temp. -80°C , polymerization time 60 mins.

^b Overall yields.

^c Controlled run, no **Inimer 1** and external additive were added.

by RI and UV detectors for selected samples. As PIB is transparent to UV, so the UV traces demonstrate **Inimer 1** only. It can be concluded from these results that **Inimer 1** can be copolymerized with isobutene.

As is shown in Table 1, in the presence of external additives, the molecular weight distribution is much narrower than that in the absence of external additives. It can also be concluded that the proton trap DtBP can suppress the initiation with moisture (about 10^{-4} – 10^{-3} M).^[19] Assuming that the initiation efficiency is 100% in the presence of DtBP, we can then calculate the molecular weight which is about 3540. Actually, the determined molecular weight of Sample HV-6 is more than twofold the theoretical value. This indicated that the **Inimer 1** plays the role as an inimer and finally forms the branched chains. Also, as is indicated in Table 1, the polymer with relatively higher molecular weight and narrower molecular weight distribution can be obtained by using pyridine as an additive.

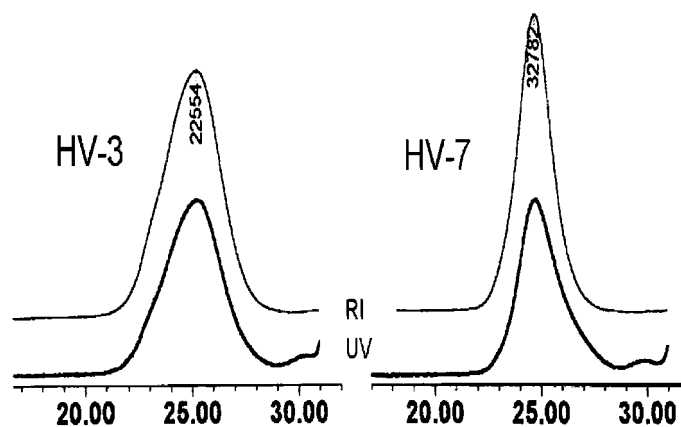
**Figure 1.** The GPC traces of typical samples of the copolymers.

Table 2. The effects of $[\text{Inimer } \mathbf{1}]_0/[\text{IB}]_0$ ratio on the copolymerization of **Inimer 1** with isobutene.^a

Sample ID	$[\text{Inimer } \mathbf{1}]_0/[\text{IB}]_0$	Yield, % ^b	\bar{M}_n	\bar{M}_w/\bar{M}_n
HV3-0 ^c	0	95.2	20800	1.66
HV3-1	0.004	96.2	31600	1.59
HV3-2	0.0075	95.9	27600	1.76
HV3-3	0.01	96.8	23800	2.01
HV3-4	0.015	98.9	19600	1.78
HV3-5	0.02	96.3	17700	1.72
HV3-6	0.025	100	12200	1.86
HV3-7	0.04	100	7636	1.85

^a $[\text{IB}]_0 = 1.29 \text{ M}$, $[\text{TiCl}_4]_0/[\text{Inimer } \mathbf{1}]_0 = 2$, $[\text{Inimer } \mathbf{1}]_0/[\text{Pyridine}] = 1$, Solvent: 15 ml $\text{CH}_2\text{Cl}_2 + 10 \text{ ml n-C}_6\text{H}_{14}$, at -80°C for 60 mins.

^b Overall yields.

^c Controlled run, no **Inimer 1** was added.

Effects of $[\text{Inimer}]_0/[\text{IB}]_0$ Ratios

Table 2 shows the results of experiments at various $[\text{Inimer } \mathbf{1}]_0/[\text{IB}]_0$, while the $[\text{IB}]_0$ and $[\text{TiCl}_4]_0/[\text{Inimer } \mathbf{1}]_0$ ratio were kept constant. With the increase of the $[\text{Inimer } \mathbf{1}]_0/[\text{IB}]_0$, the yields of the polymer are usually around 100%. Figure 2 is the dependence of \bar{M}_n on $[\text{Inimer } \mathbf{1}]_0/[\text{IB}]_0$. As is shown in Fig. 2, the molecular weights decrease with the increase of **Inimer 1**, however, it is noted that when the **Inimer 1** is at relatively lower concentration, the molecular weights decreases slightly less than that at a relatively higher **Inimer 1** concentration (Compare HV3-1–HV3-3 with HV3-5–HV3-7). This is probably due to the fact that in the relatively lower concentration of inimer **1** ($[\text{Inimer } \mathbf{1}]_0/[\text{IB}]_0 = 0.004\text{--}0.01$), the decrease of the degree of polymerization with inimer is

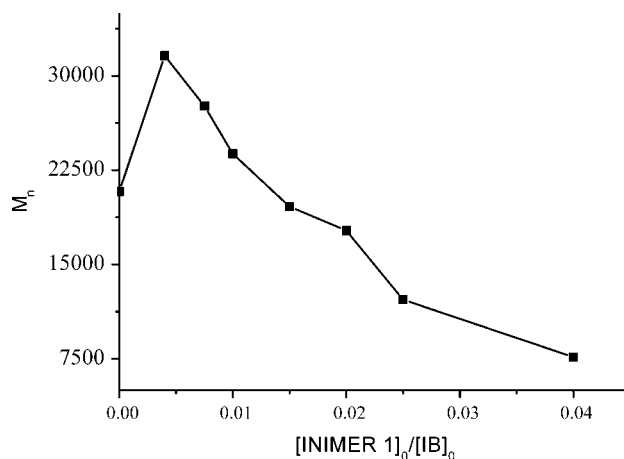


Figure 2. The \bar{M}_n dependence on the ratio of $[\text{Inimer } \mathbf{1}]_0/[\text{IB}]_0$ (conditions as in Table 2).

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Table 3. The results of the experiments specially designed for understanding the role of the **Inimer 1**.^a

Sample ID	$[\text{I}]_0/[\text{IB}]_0^{\text{b}}$	Yield, %	\bar{M}_n	\bar{M}_w/\bar{M}_n	\bar{M}_n^{c}	$\bar{M}_w/\bar{M}_n^{\text{d}}$
HV6-1	0.005	86.1	22400	1.89	NA	NA
HV6-2	0.01	86.3	16600	1.55	7620	1.67
HV6-3	0.005	87.5	18000	1.92	NA	NA
HV6-4	0.01	88.3	13500	2.14	13100	2.09
HV6-5 ^e		82.3	1740	1.47	NA	NA
HV6-6	0.20	86.8	3950	2.06	NA	NA

^aFor HV6-1–HV6-4, $[\text{IB}]_0 = 1.29 \text{ M}$, $[\text{TiCl}_4]_0 = 0.067 \text{ M}$, $[\text{Pyridine}] = 0.018$, Solvent: 10 ml CH_2Cl_2 + 10 ml $n\text{-C}_6\text{H}_{14}$, polymerization time 60 mins.

^bFor HV6-1 and HV6-2 using **Inimer 1** as initiator, for HV6-3 and HV6-4 using 2-benzenyl-propan-2-ol as the initiator.

^cIndicated the value of degradation by selective oxidation after 72 hrs.

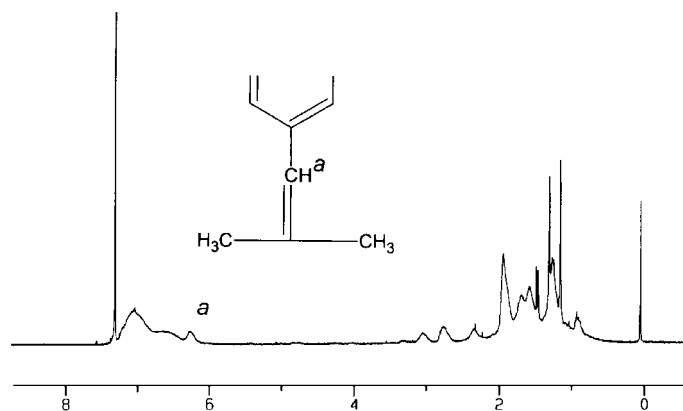
^dAs the \bar{M}_n .

^eFor HV6-5 and HV6-6 $[\text{Pyridine}]/[\text{Inimer 1}]_0 = 1$, $[\text{TiCl}_4]_0/[\text{Inimer 1}]_0 = 3$. $[\text{Inimer 1}]_0 = 0.16 \text{ M}$. No isobutene was added for HV6-5.

counterbalanced by the molecular weight of the branched chain. It should also be pointed out that the molecular weight in our experiments is universally calibrated by linear PIB. The true molecular weight may be higher than the experimental values.

The Role of the Inimer 1 in the Copolymerization

The molecular weight of polymers obtained by copolymerization of inimer with monomer is probably higher than that without inimer. In order to understand

**Figure 3.** $^1\text{H-NMR}$ spectrum of sample HV6-5.

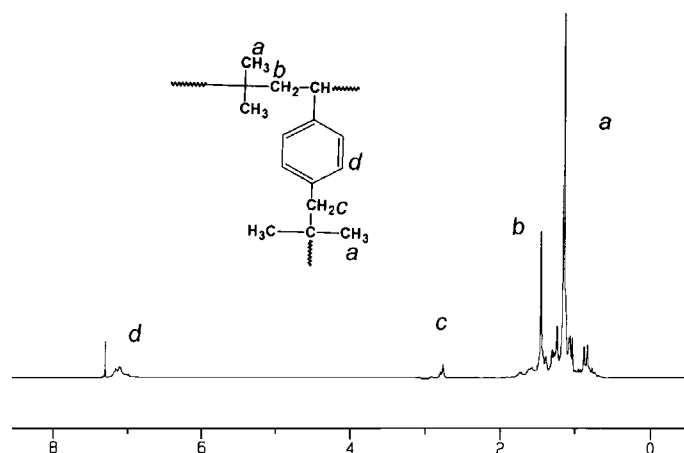
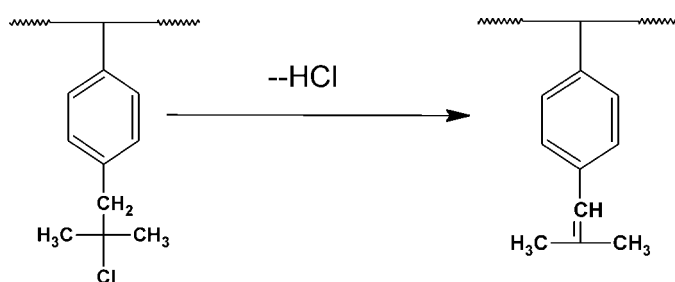


Figure 4. The $^1\text{H-NMR}$ spectrum of sample HV6-6.

the mechanism of the **Inimer 1** in the copolymerization, we used 2-benzyl-propan-2-ol as the initiator and degradation of some typical samples by selective oxidation. The results are shown in Table 3.

As is shown in Table 3, the molecular weights of polymers obtained by copolymerization of isobutene with **Inimer 1** are probably higher than that of the polymers obtained by using 2-benzyl-propan-2-ol as initiator when the other conditions remained the same. This suggested that **Inimer 1** plays the role both as a monomer and initiator. The initiating efficiencies (I_{eff}) of the 2-benzyl-propan-2-ol in the employed system are 62% and 42% for HV6-3 and HV6-4, respectively. The relatively lower I_{eff} may be due to the fact that the Lewis acid strength of TiCl_4 is too strong to match the tert-alcohol group of the **Inimer 1** to achieve the living or controlled carbocationic polymerization, i.e., the rate of initiating is much smaller than that of the chain propagation. It can be inferred that the lower branching efficiency is related to the relatively lower rate of the initiation of the tert-alcohol group of the **Inimer 1**.

Figures 3 and 4 are the $^1\text{H-NMR}$ spectra of Sample HV6-5 and HV6-6, respectively. There weren't any chemical shifts corresponding to the vinyl group of **Inimer 1** in Sample



Scheme 2. Mechanism of dehydrochlorination.

Table 4. The dependence of the \bar{M}_n and yields on the polymerization time.^a

Sample ID	Polymerization time (min)	Conversion (% wt)	\bar{M}_n	\bar{M}_w/\bar{M}_n
HBT-1	5	28.7	5050	2.67
HBT-2	10	39.7	5920	2.28
HBT-3	15	48.9	6390	2.07
HBT-4	22	65.5	7100	1.98
HBT-5	30	86.6	9870	1.83
HBT-6	60	95.5	11800	1.86
HBT-7	105	99.8	12700	1.91

^a [IB]₀ = 1.0 M, [Inimer 1]₀/[IB]₀ = 0.025, [Inimer 1]₀/[Pyridine] = 1, [TiCl₄]₀/[Inimer 1]₀ = 4/1, Solvent: 40 ml CH₂Cl₂ + 60 ml n-C₆H₁₄, overall yield temperature – 80°C.

HV6-5 and HV6-6. The δ 6.2 ppm is attributed to the endo olefinic proton probably formed by dehydrochlorination according to Sch. 2.

Dependence of the \bar{M}_n and Yields on the Polymerization of Time

The dependence of the molecular weight and conversions on the polymerization time was investigated and the results are summarized in Table 4 (The polymerizations were carried out in a reactor and samples were withdrawn at predetermined times to determine the conversions and molecular weight).

It can be seen from Table 5 that the conversion and \bar{M}_n s are increasing and the \bar{M}_w/\bar{M}_n s slightly decreasing with the increasing of polymerization time. Figure 5 is the relationship between conversion and molecular weight. It is shown in Fig. 5 that the molecular weight is increasing almost linearly with the evolution of the monomer conversion at the lower conversion and is increasing drastically at the higher conversion. The curve of the \bar{M} vs. conversion somewhat resembles the polycondensation and seems to agree with the results of Müller, etc.^[12] that were obtained in the synthesis of highly branched methacrylates by self-condensing group transfer copolymerization. These suggested that the copolymer of

Table 5. The effects of the [TiCl₄]₀/[Inimer 1]₀ on the copolymerization of IB with Inimer 1.^a

Sample ID	[TiCl ₄] ₀ /[Inimer 1] ₀	Yield (% wt)	\bar{M}_n	\bar{M}_w/\bar{M}_n
HV4-1	2	59.1	34100	1.78
HV4-2	3	62.5	33400	1.63
HV4-3	4	84.7	30100	1.83
HV4-5	6	– 100	26800	1.79

^a [IB]₀ = 1.29 M, [Inimer 1]₀/[IB] = 0.075, [Inimer 1]₀/[Pyridine] = 1, Solvent: 10 ml CH₂Cl₂ + 10 ml n-C₆H₁₄, polymerization time 90 mins, overall yield temperature – 80°C.

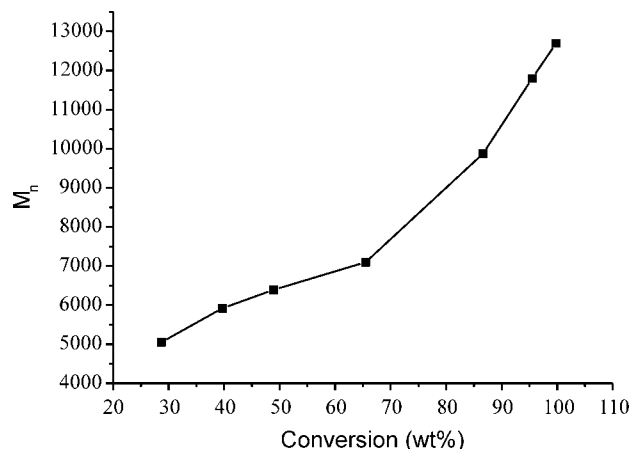


Figure 5. The relationship between molecular weight and polymerization conversion.

IB with **Inimer 1** co-initiated by TiCl_4 in presence of pyridine as electron donor is branched polymer.

The Effect of the $[\text{TiCl}_4]_0$

Table 5 shows the results of the experiments carried out at different $[\text{TiCl}_4]_0/[\text{Inimer 1}]_0$ while the $[\text{Inimer 1}]_0/[\text{IB}]_0 = 0.75\%$ (mole). It demonstrates that the molecular weights decrease, while the yields of copolymers increase with the increasing of the $[\text{TiCl}_4]_0$ and the molecular weight distributions remain almost constant. Our results are somewhat similar to the results of Puskas et al.,^[16] who used 4-(2-methoxyisopropyl) styrene as inimer. The yields of copolymers increase with increasing of $[\text{TiCl}_4]_0$ are as expected.

CONCLUSION

The carbocationic copolymerization of IB with inimer, namely 4-(2-hydroxyl-2-methylpropyl) styrene, aimed at the synthesis of highly branched polyisobutene was investigated using TiCl_4 as co-initiator in the presence of external added electron donor in mixed solvent of CH_2Cl_2 with n-hexane at -80°C . It demonstrated that the 4-(2-hydroxyl-2-methylpropyl) styrene plays the roles both as a monomer and initiator as well, and the copolymers obtained are branched polymers.

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