Macromolecules **1997,** *30,* 649−651

Coupling Reaction of Oligomeric Polyisobutylene through ω-Isopropenyl Functionality

Simion Coca and Rudolf Faust*

Polymer Science Program, Department of Chemistry,
University of Massachusetts Lowell, One University Avenue,
Lowell, Massachusetts 01854

Received August 5, 1996
Revised Manuscript Received November 8, 1996

Introduction

In-situ coupling of living polyisobutylene (PIB) has recently been accomplished using bis-diphenylethylenes (bis-DPEs) such as 2,2-bis[4-(1-phenylethenyl)phenyl]-propane and 2,2-bis[4-(1-tolylethenyl)phenyl]propane, where the two DPE moieties are separated by a spacer group.[1] Compared to the starting material, the coupled product exhibited doubled molecular weight and narrower molecular weight distribution (MWD). This process has its great importance in that rapid and quantitative coupling can be achieved independently of the chain length of the starting polymer. This could be readily applicable to the synthesis of telechelic polymers (starting with the monofunctional derivatives) and ABA type triblock copolymers (when the crossover from monomer B to monomer A is difficult). A_2B_2 star−block copolymers can also be prepared through this process since the resulting coupled product retains the living sites stoichiometrically.

While the relative amount of coupling agent is negligible in the coupling reaction of high molecular weight PIB, the above process would appear impractical for the coupling of oligomeric PIB (M_n = 1000−2000) since the relative amount of coupling agent could be too high (10−15 wt %) in the coupled product. Since Kennedy et al.[2] reported that ω-isopropenyl PIB (PIB-$CH_2C(CH_3)=CH_2$) can be easily prepared by treatment of chloro-end functionalized PIB (PIB-$CH_2C(CH_3)_2Cl$) with a base, we embarked on the coupling of oligomeric PIB through ω-isopropenyl functionality. Model reaction for the coupling of olefinic PIB could be found in the work by Hasegawa et al.[3] They reported that isobutylene tetramers (IB_4) can be obtained in high yields (80−90%) by the cationic coupling of commercial trimethylpentenes, consisting of isomers of isobutylene dimer, in the presence of oxo acid, e.g., CF_3SO_3H as catalyst, in nonpolar solvent at 0−30 °C. Unfortunately, systematic investigation was not carried out with pure 2,4,4-trimethyl-1-pentene (IB_2).

We investigated the coupling reaction of pure IB_2, which mimics ω-isopropenyl PIB, with cationic catalyst as a model reaction for the coupling of ω-isopropenyl PIB. On the basis of those results, we will discuss the coupling of olefinic PIB through ω-isopropenyl functionality.

Experimental Section

Materials. Methyl chloride (CH_3Cl) and isobutylene (IB) were dried by passing the gases through in-line gas purifier columns packed with BaO/Drierite and condensed at −80 °C prior to polymerization. Hexane was refluxed for 48 h with concentrated sulfuric acid, washed until neutral with distilled water, dried for 24 h over molecular sieves, refluxed for 24 h over CaH_2, and distilled under nitrogen atmosphere just before use. CH_2Cl_2 was purified by washing it with distilled water until neutral and drying over $MgSO_4$ overnight. It was refluxed for 24 h over P_2O_5 and distilled just before use. 2,4,4-Trimethyl-1-pentene (IB_2) (Aldrich, 99%) was distilled from CaH_2. CF_3SO_3H, $TiCl_4$ (99.9%), and 2,6-di-*tert*-butylpyridine (DTBP) were used as received from Aldrich.

Table 1. Dimerization of IB_2 with CF_3SO_3H in Hexane[a]

no.	temp (°C)	time (h)	yield (%)
1	0	0.5	93
2	0	1	100
3	0	2	100
4	rt	0.5	62
5	rt	1	73
6	rt	2	84

[a] $[IB_2]$ = 0.625 M and $[CF_3SO_3H]$ = 0.01 M; rt = room temperature.

Procedures. Tetramers of isobutylene (IB_4) were obtained by coupling of IB_2 in the presence of CF_3SO_3H using a similar procedure reported by Hasegawa et al.;[3] 0.01 M CF_3SO_3H solution in hexane was added to 0.625 M IB_2 in hexane as solvent at a different reaction temperature. The extent of the coupling and the structure of the products were determined by GC−MS and ^1H NMR, repectively.

Chloro-end functionalized PIB (PIB-$CH_2C(CH_3)_2Cl$) was prepared by the 2,4,4-trimethyl-2-chloropentane (TMPCl)/BCl_3/IB/DTBP/CH_3Cl/−40 °C system in an MBraun 150M stainless steel glovebox. This PIB-$CH_2C(CH_3)_2Cl$ (M_n ~ 500 or 1000) was converted to ω-isopropenyl PIB (PIB-$CH_2C(CH_3)=CH_2$) using a similar procedure reported by Kennedy et al.[2] ^1H NMR spectrum of the products indicated 100% dehydrochlorination to the exo-olefin. Resonances at 4.58 and 4.78 ppm are assigned to -CH_2-$C(CH_3)=CH_2$, while resonances at 1.93 and 1.75 ppm are associated with -CH_2-$C(CH_3)=CH_2$ and -CH_2-$C(CH_3)=CH_2$ protons, respectively.[2,4] Coupling reaction of ω-isopropenyl PIB was carried out using an analogous method used in the coupling reaction of IB_2 in the presence of CF_3SO_3H as catalyst.

Characterizations. The coupled product (IB_4) of IB_2 was characterized by the Hewlett-Packard gas chromatography−mass spectrometry system consisting of a Model 5890 series II gas chromatograph, a Model 5971A mass selective detector equipped with a 59822B HP ionization gauge controller, and an HP G1030A MS Chemstation (Avondale, PA). Helium (99.999%) was used as a carrier gas at 0.9 mL/min.

Molecular weights of PIB before and after the coupling reaction were measured using a Waters HPLC system equipped with a Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/vis detector, on-line multiangle laser light scattering (MALLS) detector (miniDAWN, Wyatt Technology Inc.), Model 712 sample processor, and five ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The flow rate of THF was 1.0 mL/min. The absolute molecular weights and molecular weight distributions were determined based on the MALLS and refractive index detector signals using the ASTRette software. For PIB a refractive index increment (d*n*/d*c*) of 0.96 mL/g was used.

Results and Discussion

Coupling Reaction of 2,4,4-Trimethyl-1-pentene (IB_2). Lower than quantitative yields of IB_4 were reported in the coupling of commercial trimethylpentenes by Hasegawa and Higashimura.[3] This can be attributed to the presence of IB_2 isomers other than 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene in the feed, all of which dimerized much more sluggishly than the latter two isomers. (2,4,4-Trimethyl-2-pentene, which is unable to dimerize due to steric hindrance, first isomerized to 2,4,4-trimethyl-1-pentene which subsequently dimerized.) Therefore we reinvestigated the dimerization of pure 2,4,4-trimethyl-1-pentene (IB_2) in the presence of catalytic amounts of CF_3SO_3H in hexanes as solvent at 0 °C and at room temperature. The results are summarized in Table 1.

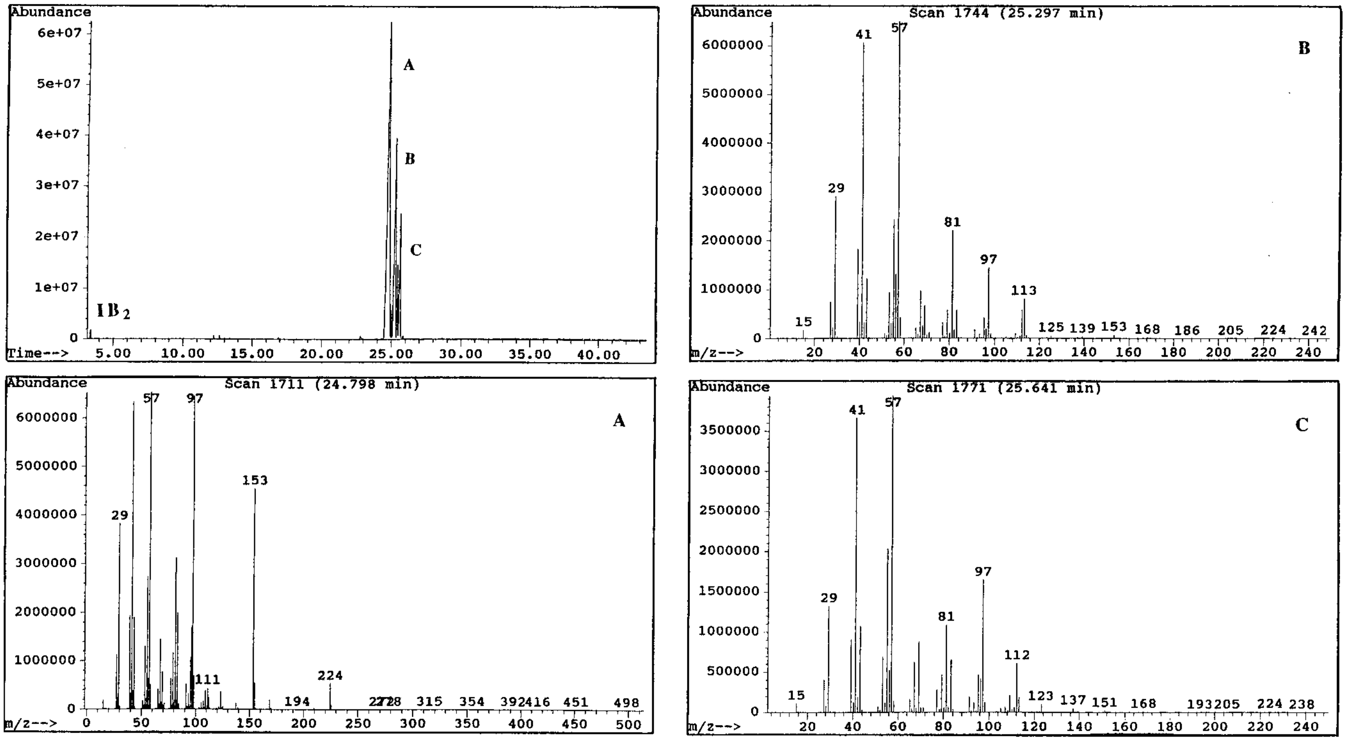
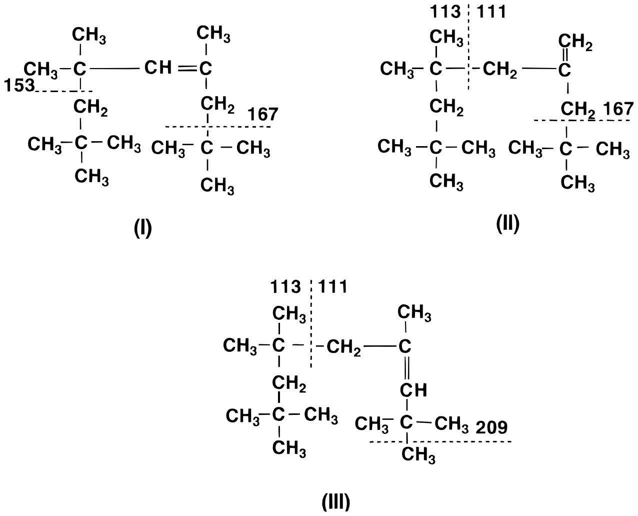


Figure 1. Gas chromatogram of the product of IB_2 dimerization (upper left) and mass spectra of the main components (A−C) obtained in hexane at 0 °C.

Chart 1. Fragmentation Pattern of the Three Possible IB_4 Isomers



At 0 °C dimerization is complete after 1 h, without any byproduct. Higher oligomers (mainly trimers of IB_2), reported by Hasegawa et al. in small amounts, were not observed under these reaction conditions. At room temperature, the yield is lower due to the appearance of higher oligomers. The products were characterized using ^1H NMR and GC−MS spectroscopy. The ^1H NMR spectra showed the expected signals at 4.85 ppm (CH_2=C) and 5.2 ppm (C*H*=C). Gas chromatography of the product obtained at 0 °C also indicated complete dimerization and the presence of three main product components (A−C) in an approximate ratio of 3:2:1 (upper left in Figure 1). Components A−C were further analyzed by mass spectrometry and identified as isomers of IB_4 with structures I−III, respectively, as shown in Chart 1. This is in contrast to results reported by Hasegawa et al. identifying two C16 isomers as the main products.

Coupling Reaction of ω-Isopropenyl PIB. On the basis of the results obtained with IB_2 as a model compound, we commenced to study the coupling of oligomeric PIB through ω-isopropenyl functionality ($-CH_2C(CH_3)=CH_2$) under identical conditions. ω-Isopropenyl PIBs (PIB-$CH_2C(CH_3)=CH_2$) with M_n = 500 and 1000 g/mol were used in the coupling reaction. Unexpectedly, at 0 °C dimerization was absent with both samples. Instead of the expected higher molecular weights, the products exhibited lower molecular weights, most probably due to cracking.[5] This is accentuated at room temperature and in the presence of high concentrations of oxo acid.

We postulated that lower temperature would be necessary to effect coupling due to an even more unfavorable entropy change with oligomeric PIB compared to IB_2. The effect of the reaction temperature was studied at different concentrations of triflic acid in hexane or CH_2Cl_2 at 0, −30, and −80 °C. According to the results, coupling was absent in CH_2Cl_2 as solvent at all three temperatures. In many cases the MWDs were bimodal and shifted to lower molecular weight indicating cracking. Coupling was also absent in hexanes at 0 and −30 °C at low concentrations of triflic acid, since the molecular weight of the product was identical with that of the starting material. Under the same conditions but at a higher concentration of triflic acid, the MWD became broader and shifted to lower molecular weight and the polymer became UV active (at the 254 nm detection wavelength), suggesting the formation of highly substituted olefin.

At −80 °C, using a low concentration of triflic acid, coupling of ω-isopropenyl PIB proceeded, and the extent of coupling increased with time (Figure 2), reaching ~70% after 6 h. The polymer also became UV active. At a higher concentration of CF_3SO_3H (=0.1 M), however, bimodal MWD shifting toward lower molecular weight was obtained.

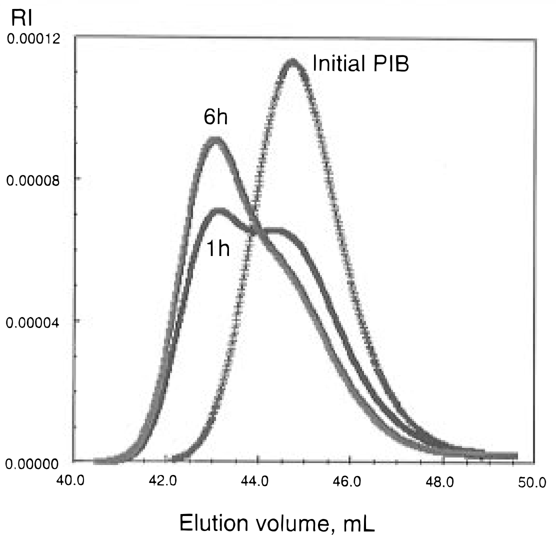


Figure 2. GPC RI traces of the initial PIB and the products of coupling after 1 and 6 h reaction time. Reaction conditions: [PIB] = 0.1 M and [CF_3SO_3H] = 0.01 M in hexane at −80 °C.

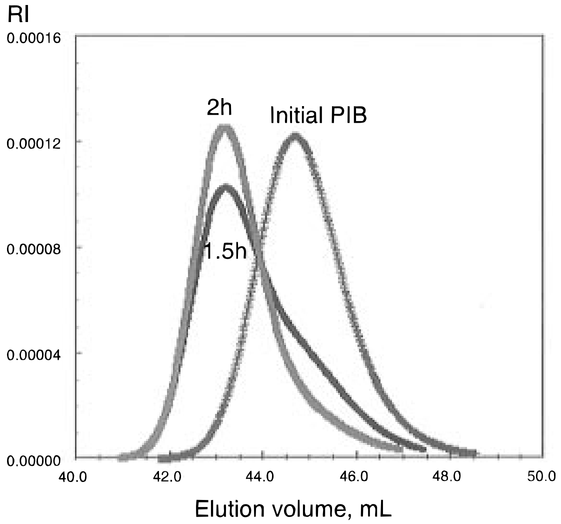


Figure 3. GPC RI traces of the intial PIB (M_n = 1050, M_w/M_n = 1.11) and the products of coupling after 1.5 h (M_n = 1600, M_w/M_n = 1.28) and 2 h (M_n = 2120, M_w/M_n = 1.04). Reaction conditions: [PIB] = 0.4 M and [CF_3SO_3H] = 0.01 M in hexane at −80 °C.

Since coupling is expected to be a second-order reaction with respect to ω-isopropenyl PIB, the rate of coupling may be increased by increasing the concentration of ω-isopropenyl PIB. Thus experiments were carried out by increasing the concentration of ω-isopropenyl PIB to 0.4 and 0.5 M. The GPC traces of the products obtained are shown in Figures 3 and 4, which demonstrate that quantitative coupling of ω-isopropenyl PIB can be achieved in nonpolar solvent at −80 °C by using 0.5 M (after 1.5 h) or 0.4 M (after 2 h).

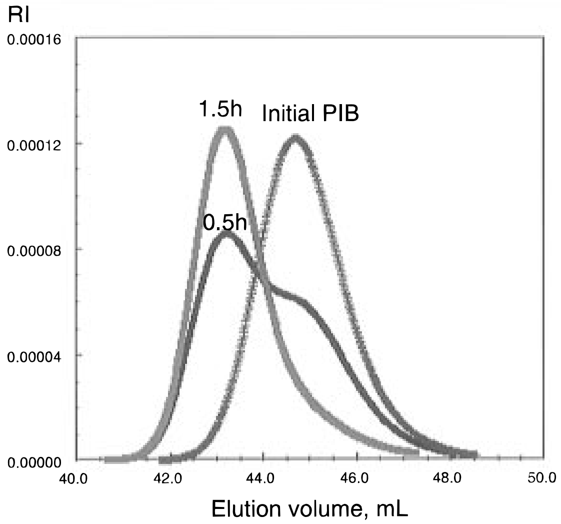


Figure 4. GPC RI traces of the initial PIB (M_n = 1050, M_w/M_n = 1.11) and the products of coupling after 0.5 h (M_n = 1700, M_w/M_n = 1.22) and 1.5 h (M_n = 2160, M_w/M_n = 1.04). Reaction conditions: [PIB] = 0.5 M and [CF_3SO_3H] = 0.01 M in hexane at −80 °C.

Conclusions

Quantitative coupling of IB_2 and ω-isopropenyl PIB was accomplished by using CF_3SO_3H as catalyst. The experimental conditions (solvent, temperature, and catalyst concentration), however, greatly influence the outcome of the coupling reaction. A nonpolar solvent, e.g., hexane, and low concentrations of the catalyst, CF_3SO_3H, are necessary to avoid side reactions such as cracking. While coupling of IB_2 proceeds rapidly to completion at 0 °C, coupling of ω-isopropenyl PIB was only achieved at −80 °C.

Acknowledgment. Partial financial support by the National Science Foundation (DMR-9502777) is gratefully acknowledged. We are also grateful to Dr. Yongkyung Kim for the GC−MS measurements.

References and Notes

(1) (a) Bae, Y. C.; Coca, S.; Canale, P. L.; Faust, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (1), 369. (b) Bae, Y. C.; Fodor, Zs.; Faust, R. *Macromolecules,* in press.
(2) Kennedy, J. P.; Chang, V. S. C.; Smith, R. A.; Ivan, B. *Polym. Bull.* **1979**, *1*, 575.
(3) Hasegawa, H.; Higashimura, T. *J. Appl. Polym. Sci.* **1982**, *27*, 171.
(4) Si, J.; Kennedy, J. P. *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 2011.
(5) Kennedy, J. P.; Rengachary, S. *Adv. Polym. Sci.* **1974**, *14*, 1.

MA9611681