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Multi-arm star polyisobutylenes

1. Synthesis and proof of structure

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Summary

The first synthesis of a multi-arm radial-star polyisobutylene (∗-PIB) is described. The synthesis occurred by the addition of excess divinylbenzene (DVB) linking reagent to a living polyisobutylene ($PIB^{\oplus}$) charge i.e., by the "arm first" method under specific conditions. The radial structure of the ∗-PIB was proven by determining the molecular weight of a sample by light scattering, then selectively destroying the aromatic polydivinylbenzene (PDVB) core, and finally determining the molecular weight of the surviving aliphatic PIB arms. The synthesis strategy, kinetic observations during synthesis, and procedures leading to a representative ∗-PIB are described. This product whose $\overline{M}_w$=1,134,400 g/mole with $\overline{M}_w/\overline{M}_n$=2.83, contained ~90.3 mole% (~78 wt.%) PIB arms and ~9.7 mole% (~22 wt.%) aromatic core; thus the number of PIB arms emanating from the core was $\overline{N}_{n,arm}$ (number average number of arms)=56 or $\overline{N}_{w,arm}$ (weight average number of arms)=110.

I. Introduction

Multi-arm radial-star polymers are of great practical and theoretical interest. Since the late sixties a large number and variety of such radial-star homo- and block polymers have been prepared, mainly by anionic techniques, including star polystyrenes [1, 2], polybutadienes [3, 4], poly(*tert*-butyl acrylates) [5], poly(ethylene oxides) [6], polyisoprenes [7], and various hetero-arm stars [8, 9]. Japanese investigators have described the cationic synthesis of radial-star poly(alkyl vinyl ethers) [10, 11]. Our research concerning three- and four-arm star PIBs by direct initiation has been published [12, 13]. Recently we have initiated investigations toward the synthesis of heretofore unavailable ∗-PIBs. This publication concerns our initial results, specifically, the outline of our synthetic strategy, analytical methodology, and the results of a representative series of experiments the analysis of which demonstrates the convenient synthesis of ∗-PIB.

II. Experimental

Materials

$TiCl_4$, 2,4,4-trimethyl-1-pentene (TMP), triethylamine (TEA), CCl_4, and $SnCl_2$ were from Aldrich Chemical. CH_2Cl_2, hexanes (Hex), HCl, 30% H_2O_2, MeOH, and Et_2O were from Fisher Scientific. Hex and CH_2Cl_2 were refluxed under a N_2 atmosphere over-night and distilled from CaH_2. The synthesis of 2-chloro-2,4,4-trimethylpentane (TMPCl) and purification of TEA have been described [14]. Trifluoroacetic acid (TFA) was from Eastman Kodak Co. "High Purity" DVB, a mixture of 80.7% DVB (2.2:1 meta:para isomers) and 18.5% ethylvinylbenzene (EVB) (1.34:1 meta:para isomers) was provided by The DOW Chemical Company (composition by GC, provided by the manufacturer). The DVB was used after removing the inhibitor by column chromatography using a *tert*-butylcatechol column.

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Equipment

A Waters Co. GPC assembly equipped with RI and UV detectors was used (Waters 410 Differential Refractometer, 440 Absorbance Detector, WISP 7103, Nelson Analytical Interfaces). We also used a Waters 150-CV GPC with a RI and a multi-angle laser light scattering detector (Dawn F, Wyatt Technology Corporation). Molecular weight determinations by the use of these equipments have been described [14, 15, 16].

Procedures

A. Polymerization

A representative experiment for the synthesis of *-PIB was carried out as follows: Living isobutylene (IB) polymerization was induced by the TMPCl/$TiCl_4$ initiating system and TEA as the electron pair donor [14]; [IB]=0.89 mole/L [TMPCl]=$2 \cdot 10^{-1}$mole/L, [$TiCl_4$]:[TMPCl]=18:1, [TEA]:[TMPCl]=1:1, in 20 mL CH_2Cl_2:Hex=50:50 (vol.) solution at -40°C. Reactions were performed in series of manually agitated large test tubes (~75 mL) under N_2 atmosphere in a "dry box" [14, 15]. Upon the introduction of $TiCl_4$ the charge turned pale yellow. The intensity of the color increased slowly as the reactions progressed. Livingness, rates, and reproducibility of IB polymerization were ascertained in dedicated experiments. At ~95% IB conversion DVB (2 mL of 1.0 mole/L DVB in CH_2Cl_2:Hex=50/50) was added dropwise rapidly to the living $PIB^{\oplus}$ charges. Thus [DVB]:[TMPCl]=10:1 or [DVB+EVB]:[TMPCl]=12.5. Orienting experiments showed that a 10 fold molar excess of DVB over TMPCl produces multi-arm *-PIB with very little (~3%) PIB contamination (see also later). The exact time of the addition of the linking agent is of significance: DVB addition at lower than ~95% IB conversion leads to undesirable IB/DVB copolymers and ill-defined low molecular weight product, whereas DVB addition after 100% IB conversion may result in the loss of activity of $PIB^{\oplus}$ [17]. Upon DVB addition, the pale yellow living $PIB^{\oplus}$ charge immediately turned dark orange suggesting rapid $PIB^{\oplus} + DVB \rightarrow PIB\text{-}DVB^{\oplus}$ cross-over. The intensity of this color slightly diminished after long (>90 hrs) reaction times. The charges were transparent, homogeneous and filterable without residue (for GPC determination). The reactions were terminated by the addition of 2 mL prechilled MeOH at 1/4, 1/2, 1, 2, 3, 18, 48, and 96 hrs after DVB introduction. After quenching the charges into excess MeOH, the solvents were evaporated. The residues were extracted with ~50 mL HCl (10% aqueous), and subsequently 3 times with ~50 mL MeOH; the supernatant solutions were decanted, and the products dried in vacuo at ambient temperature for a week. The products were analyzed by gravimetry (yield, conversion) and GPC equipped with RI, UV, and/or LS detectors (molecular weight, hydrodynamic volume).

B. Core Destruction

A representative core destruction experiment was carried out as follows [12, 18]: Half a gram of *-PIB was dissolved in 50 mL CCl_4 in a 250 mL round bottom flask equipped with a Teflon coated magnetic stirring bar. Under stirring first 50 mL TFA and subsequently 25 mL 30% H_2O_2 were added dropwise to the charge. The homogeneous charge was refluxed (67°C) and ~1 mL samples were withdrawn by Pasteur pipettes into test tubes at 0, 1/2, 1, 2, 4, 7, and 23 hrs. The excess in situ formed trifluoroperacetic acid was destroyed by adding 1 mL of 10 wt.% aqueous $SnCl_2$ solutions. The samples (heterogeneous mixtures of yellow oil and colorless solid) were dried in vacuum at ~40°C for ~3 hrs, 10 mL water were added and the heterogeneous system was extracted with Et_2O (10 mL) for 16 hrs. The ether phase was separated by siphoning off by a Pasteur pipette, dried over $MgSO_4$ for 24 hrs, and analyzed by GPC.

Similar experiments (controls) have also been carried out with PIB and PDVB homopolymers.

C. Light Scattering

One mg *-PIB was dissolved in 1 mL of freshly distilled THF and 250 μL of this solution were injected into the GPC instrument equipped with the LS detector; λ=632.8 nm, dn/dc=0.126 cm^3/g.

III. Synthetic Strategy

Scheme 1 outlines the strategy used to synthsize *-PIBs. The synthesis starts by the living polymerization of IB (Step 1, Scheme 1). Details of these reactions have been extensively discussed elsewhere [14, 19, 20, 21].

The next step is the addition of the DVB linking agent to the living PIB$^{\oplus}$ charge to effect the PIB$^{\oplus}$ + DVB $\rightarrow$ PIB-DVB$^{\oplus}$ crossover (Step 2, Scheme 1). The scheme shows the various resonance structures expected from para and meta DVB. We disregard reactions with para and meta EVB because EVB does not lead to linking. The incorporated EVB merely increases the size of the cores.

The subsequent event is core growth, which is in fact DVB homopolymerization (Step 3, Scheme 1). Since the concentration of DVB must be in excess in respect to the living PIB$^{\oplus}$s more than one DVB molecule is expected to add to the growing ~DVB$^{\oplus}$. We do not formally indicate intra- and intermolecular reactions between DVB$^{\oplus}$ plus unreacted -C_6H_4-CH=CH_2 but such reactions may occur.

After and/or simultaneously with core growth, intermolecular linking to multi-arm stars proceeds by living PIB$^{\oplus}$ or PIB-DVB$^{\oplus}$ (Steps 4.a. and 4.b. Scheme 1). Both species can react with -C_6H_4-CH=CH_2 groups except when they are terminal (i.e., -CH_2-CH$^{\oplus}$-C_6H_4-CH=CH_2). The reason for the reluctance of PIB$^{\oplus}$ or PIB-DVB$^{\oplus}$ to react with the latter species is due to resonance and inductive effects: Both resonance and inductive effects will prohibit reaction with the p-DVB$^{\oplus}$ terminus, while the inductive effect will prevent reaction with m-DVB$^{\oplus}$ (see symbolism; Step 2 and 3, Scheme 1).

Ultimately, various intramolecular cyclizations, intermolecular star-star linkings, etc. are also expected occur (Step 5, Scheme 1) because numerous -C_6H_4-CH=CH_2 groups and active cations are still present in the core. Intramolecular cyclization should be relatively fast and lead to microgel in the core, whereas intermolecular star-star linking would be relatively slower due to reduced interdiffusion and steric hinderance.

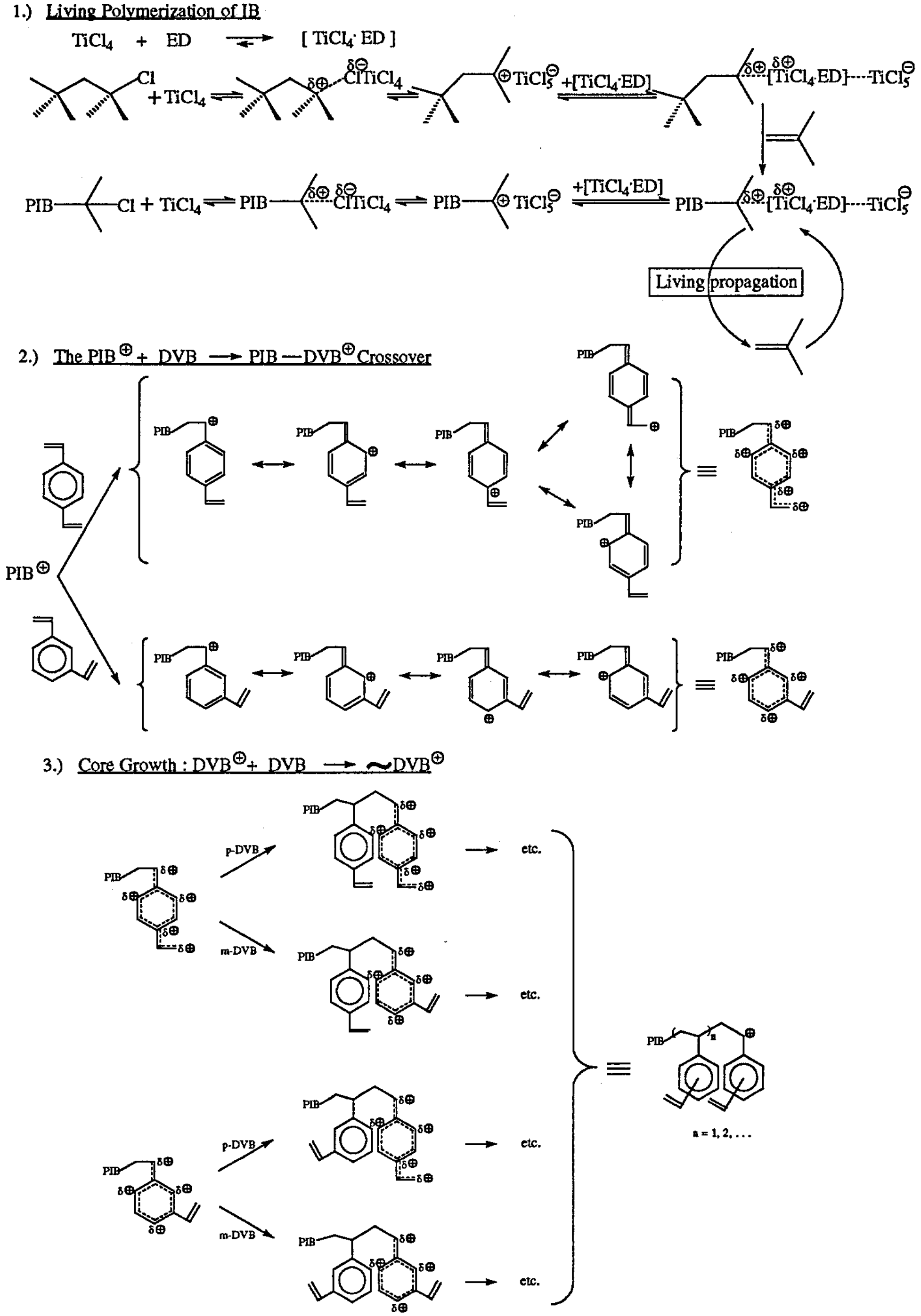
The simultaneous consideration of these events helped us greatly in designing our experiments and interpreting the results.

IV Results and Discussion

A. *-PIB Characterization by GPC

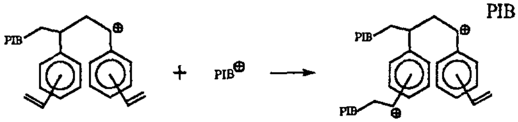
A large number and variety of orienting synthetic, kinetic, and characterization experiments have been carried out. Among the many synthetic possibilities examined good yields and relatively uncontaminated *-PIBs have been obtained by the procedure described in the Experimental. Figures 1 and 2 summarize, respectively, RI (GPC) traces and kinetic information collected in the course of a series of experiments. The 0 hr RI trace reflects the living PIB$^{\oplus}$s just before DVB addition ($V_e \approx$ 36.5 mL corresponding to $\overline{M}_n$=6,500 g/mole with $\overline{M}_w/\overline{M}_n$=1.23). This "PIB peak", although relatively diminished, remains clearly visible in all the later RI traces as well. The RI and UV (GPC) traces (latters not shown) of the 1/2, 2, and 3 hrs samples were very similar suggesting that the prominent shoulders at $V_e \approx$ 33.5, 33.3, and 33.0 mL respectively, were due to *-PIB formation by Steps 1-4 of Scheme 1. The small shift towards higher molecular weights of the 1/2 hr PIB peak

Scheme 1. Synthetic Strategy

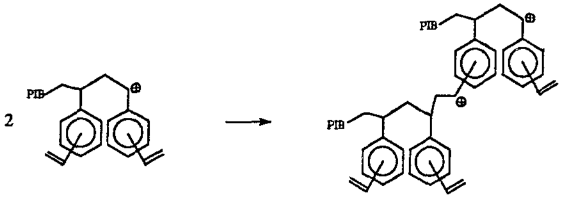


4.) Intermolecular Linking to Multi-Arm Star

a.) with $\mathrm{PIB}^{\oplus}(\mathrm{PIB{-}DVB} + \mathrm{PIB}^{\oplus} \longrightarrow \underset{\mathrm{PIB}}{\underset{|}{\mathrm{PIB{-}DVB}^{\oplus}}})$

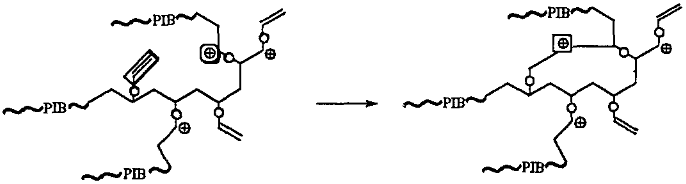


b.) with $\mathrm{PIB{-}DVB}^{\oplus}(\mathrm{PIB_1{-}DVB} + \mathrm{PIB_2{-}DVB}^{\oplus} \longrightarrow \underset{\mathrm{DVB{-}PIB_2}}{\underset{|}{\mathrm{PIB_1{-}DVB}^{\oplus}}})$



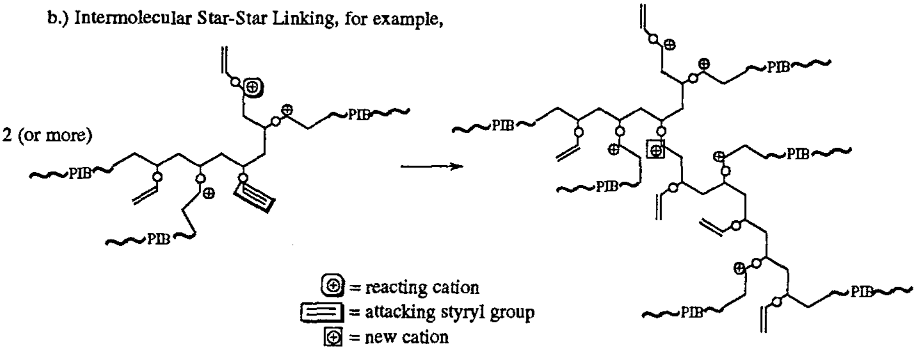
5.) Various Intramolecular Cyclizations Leading to (a) Microgel in the Core and (b) Intermolecular Star-Star Linking

a.) Intramolecular cyclizations, for example,



and similar microgels

b.) Intermolecular Star-Star Linking, for example,



and similar "secondary" stars

is most likely due to the progressing addition of DVB units to PIB$^{\oplus}$ segment. These DVB containing chains start to form stars by linking (Steps 3 and 4, Scheme 1), whereas the PIB⊕s that have not added DVB units remain unchanged and the corresponding GPC peak shifts back to its starting position V_e≈36.5 mL). Because of the absence of calibration values we have refrained assigning molecular weight values to the V_e peaks. The second shoulder at V_e≈ 31.7 mL in the 3 hrs RI trace is most likely due to secondary stars arising by intermolecular star-star coupling, i.e., by Step 5 of Scheme 1. The RI and UV traces (latters not shown) of the 18-, 48-, and 96-hrs samples were virtually identical in the V_e= 27-37 mL range which is evidence for the overall similarity and uniformity of the samples arising at long reaction times. Since the hydrodynamic volumes of multi-arm stars are insensitive to even relatively large molecular weight changes, the small but definitive shift of peaks toward lower values (i.e., from V_e≈31 to ~30 mL) of the 18-, 48-, and 96-hr GPC traces are viewed as strong indication for substantial molecular weight increase by slow intermolecular star-star linking (Step 5, Scheme 1).

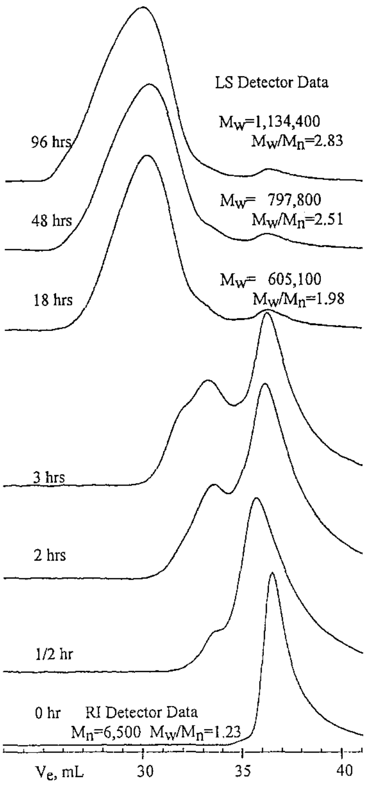


Figure 1. RI Traces of *-PIBs versus Elution Volume and Reaction Time

Table. 1. Data to Calculate N_{arm} of a *-PIB. (Data in parentheses are very crude approximations obtained by using calibration valid for linear PIB (see text).

Time, hours	M_n g/mole	M_w g/mole	M_w/M_n
0	(165,500)	(279,000)	(1.68)
0	401,050*	1,134,400*	2.83*
0.5	(85,250)	(153,450)	**
1.0	(8,300)	(53,500)	**
2.0	(8,000)	(15,650)	(1.96)
4.0	(7,500)	(9,300)	(1.24)
7.0	6,600	8,250	1.25
23.0	6,500	8,000	1.23

* by light scattering; all other data by RI (GPC)
** bimodal distribution

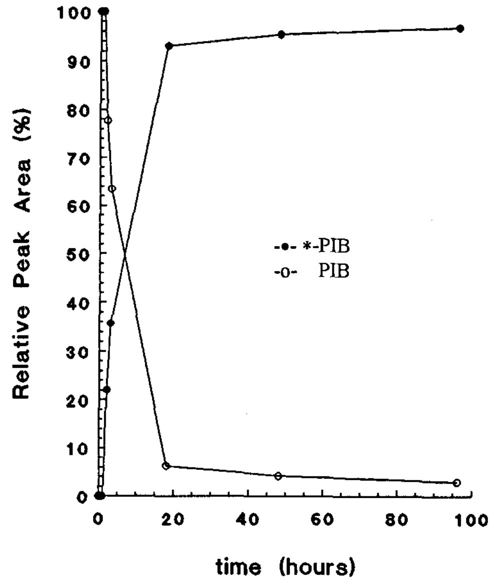


Figure 2. RI Peak Areas (%) of representative *-PIBs and PIBs obtained

Figure 2 shows relative RI (GPC) peak areas reflecting *-PIB formation (•) and PIB$^{\oplus}$ disappearance (o) as a function of time. As anticipated, the rates of *-PIB formation and PIB$^{\oplus}$ disappearance are exactly the same. The sharp break in the rates at ~18 hrs indicates a change in these mechanism: We postulate that in this range intermolecular star-star linking (Step 5, Scheme 1) becomes rate controlling. In contrast to relatively fast intermolecular arm-core linking (Step 4, Scheme 1), intermolecular star-star linking (Step 5, Scheme 1) is expected to be quite slow because of the difficult contact between individual active cores surrounded by dense inert PIB coronas.

B. Homopolymerization of DVB

Experiments have also been performed to gain insight into the homopolymerization of DVB, modeling of Step 3, Scheme 1. These experiments were carried out under conditions used for the synthesis of $*$-PIB, expect the initiator for DVB polymerization was not living $\mathrm{PIB}^{\oplus}$ but its model, $\mathrm{TMP}^{\oplus}$. These experiments invariably gave discolored insoluble tightly-gelled PDVBs which where not further characterized. Importantly, however, the PDVB gel when subjected to "core destruction" (see Experimental) gave non-detectable residues in ether.

C. Proof of Structure and Number of Arms of a $*$-PIB: Molecular Weight Determination Combined with Core Destruction

It is difficult to obtain *direct* proof of a star polymer. In most cases, e.g., with polystyrene and polybutadiene stars, the proof is often indirect and rests on various circumstantial evidences one of which is, invariably, the expectation that the chemical reactions used for the synthesis are in fact taking place as planned. In the case of $*$-PIBs, a molecule in which multiple PIB arms are attached to a largely[1] PDVB core, the presence of radial structure can be proven directly by the following sequence of steps:

1.) Determining the absolute molecular weight (for example by light scattering) of a sample which on the basis of the synthetic strategy used is expected to be a radial $*$-PIB,
2.). Selectively destroying the aromatic core which ties together the aliphatic PIB arms, and finally,
3.) Determining the molecular weight of the surviving PIB fragments. By dividing the molecular weight of the original $*$-PIB into that of the surviving PIB arms, we obtain the number of arms. Specifically, by dividing the number or weight average molecular weights of the sample ($\overline{M}_{\mathrm{n},*\text{-PIB}}$ or $\overline{M}_{\mathrm{w},*\text{-PIB}}$) into the number or weight average molecular weights of the surviving PIB arm ($\overline{M}_{\mathrm{n,PIB}}$ or $\overline{M}_{\mathrm{w,PIB}}$) respectively, we derive the number average and weight average number of arms: $N_{\mathrm{n,arm}}$ and $N_{\mathrm{w,arm}}$.

The radial structure of three-arm PIB stars, i.e., in which three PIB arms are held together by a central aromatic ring ("core"), has been proven by this methodology in our laboratories a few years ago [12, 18]. In the present instance we have used the same procedure to destroy the PDVB core of a $*$-PIB (see Experimental for details).

Experiments have also been carried out to study the kinetics of core destruction. It was found that the PDVB core of $*$-PIB is completely destroyed in ~7 hrs under our conditions. Control experiments showed that PIB ($\overline{M}_{\mathrm{n}}$=7,200 and 14,200 g/mole) survives conditions far more aggressive (refluxing for 236 hrs) than those used for core destruction, and that PDVB yields non-detectable residues in ether (see also Section IV.B.).

Table 1 summarizes pertinent results. Evidently the molecular weight of the sample decreases with increasing refluxing time and after ~7 hrs a limiting molecular weight i.e., the molecular weight of the linear PIB arm, is reached. Since GPC calibration data for $*$-PIB molecular weights do not exist, the numbers in columns 2-4 merely reflect a decrease in the size (hydrodynamic volume) of the sample. In contrast, the last two data points at 7 and 23 hrs when

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[1] The core is largely but not exclusively PDVB because even "High Purity" DVB contains ~18.5% EVB (see Experimental) which copolymerizes with DVB and thus becomes part of the core. This contribution to the core, however, can be neglected because the EVB does not sustain linking reactions.

destruction is complete, reflect the true $\overline{M}_n$'s of the surviving linear PIB arms ($\overline{M}_n$= 6,600 and 6,500 g/mole).

The following simple calculation yields $\overline{N}_{n,arm}$ and $\overline{N}_{w,arm}$. According to these data, $\overline{M}_{n,PIB}$ of the surviving PIB arms after core destruction was 6,500 g/mole (Table 1) which is equivalent to $\overline{DP}_{n,PIB}$=116. The number of moles of aromatic moieties added (and completely consumed) per PIB arm were 12.5 (see Experimental). Thus the *-PIB contained (116/128.5)×100=~90.3 mole% (~78 wt.%) PIB and ~9.7 mole% (~22 wt.%) aromatic core. In other words, the $\overline{M}_{n,*\text{-}PIB}$=401,050 g/mole (see Table 1) contained $\overline{M}_{n,PIB\ in\ star}$=362,150 g/mole plus $\overline{M}_{n,aromatic\ core}$=38,900 g/mole, or the $\overline{N}_{n,arm}$=(401,050 × 0.903)/6,500=56 PIB arm/star. Similarly, $\overline{N}_{w,arm}$=(1,134,400 × 0.78)/8,000=110. Since the $\overline{M}_{w,*\text{-}PIB}$ and $\overline{M}_{w,arm}$ values were determined by LS and RI (GPC) techniques, respectively, we consider $N_{w,arm}$ to be reliable. In contrast, the $\overline{M}_{n,*\text{-}PIB}$ value may be less accurate because it was calculated from $\overline{M}_{w,*\text{-}PIB}$ and using a rather broad molecular weight distribution ($\overline{M}_w/\overline{M}_n$=2.83). Research is continuing in this fascinating new field.

Acknowledgments

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