Macromolecules **2001,** *34,* 9−13

Articles

Step−Growth Polymers Derived from Indene and Decafluorobiphenyl. A New Polymerization Mode for Indene

Paul A. Deck* and Carrie R. Maiorana[1]

Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061-0212

Received August 14, 2000; Revised Manuscript Received November 9, 2000

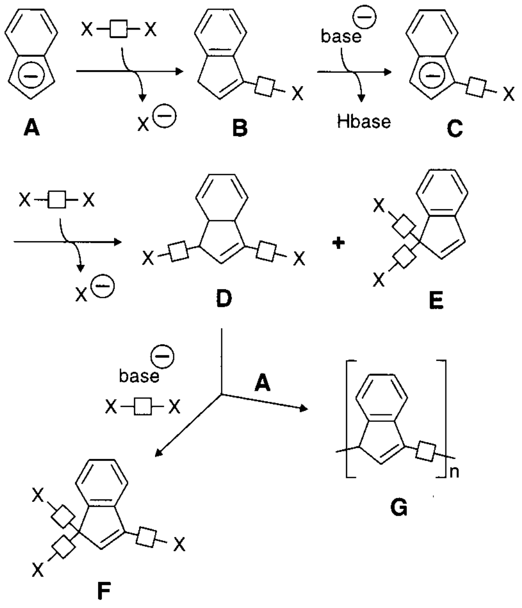
ABSTRACT: Whereas indene typically polymerizes by 1,2-addition to the olefin, sodium indenide and decafluorobiphenyl react in the presence of sodium hydride in THF to afford a step−growth polymer in which indene is connected via the 1- and 3-positions by 4,4′-octafluorobiphenylene units. The toluene-soluble fraction of the polymer product showed $M_n = 3500$ and $M_w = 5700$. The corresponding number-averaged degree of oligomerization of about 10 was confirmed by NMR end group analysis. Abstraction of the remaining acidic indenyl protons using sodium hydride followed by treatment of the deep magenta intermediate with $Mn(CO)_5Br$ in THF affords an organometallic polymer in which $Mn(CO)_3$ fragments are bonded in a pentahapto fashion to the indenyl groups of the 1,3-indenylene-4,4′-octafluorobiphenylene repeat unit.

Introduction

Indene and styrene typically polymerize by vicinal addition at the olefin through either free-radical or "living" cationic mechanisms.[2] Unlike styrene, however, indene does not undergo facile anionic polymerization. In principle, the allylic delocalization of the indenyl anion could be exploited in condensation polymerization (Scheme 1) by forming new bonds to the 1- and 3-positions. To achieve linear, regioregular polymers (**G**), such a scheme would need to satisfy three main criteria. First, the monosubstituted indene (**B**) formed upon reaction of the indenyl anion (**A**) with a difunctional electrophile (**X**−□−**X**) must be deprotonated to afford the reactive intermediate (**C**), while avoiding side-reactions between the electrophile (□−**X**) and the base. Second, the process must be regioselective for 1,3-disubstitution (**D**), because 1,1-disubstituted indene intermediates (**E**) would become chain kinks. An example of the tendency toward 1,1-disubstitution is found in the reaction of indenes with silicon halides to give 1,1-disilylated indenes.[3] Third, the disubstituted intermediates (**D**) must not oversubstitute to afford 1,1,3-trisubstituted indenes (**F**),[4] which would introduce branches or cross-links. These selectivity issues suggest the need for an *electron-withdrawing* linker (□) that will attenuate the nucleophilicity of the neighboring indenyl carbanion after bond formation.

We showed earlier that sodium indenide reacts with hexafluorobenzene to afford either **H** or **J**, depending on the reaction conditions.[5] Neither the 1,1-disubstituted isomer nor the trisubstituted congener of **J** was observed. Subsequently, we found that decafluorobiphenyl reacts with 2 equiv of sodium cyclopentadienide (NaCp) to afford **K**.[6] Others have used perfluoroaromatic compounds as difunctional electrophiles in step−growth syntheses of poly(arylene ethers).[7] On the basis of these precedents, we speculated that indene and decafluorobiphenyl might be suitable partners for a step−growth polymerization of the type outlined in Scheme 1. We now report that indene reacts with 1.0 equiv of decafluorobiphenyl in the presence of excess sodium hydride (base) to afford a linear, regioregular polymer. We describe the fractionation of this new substance and the characterization of the toluene-soluble fraction by combinations of ^{1}H NMR, ^{19}F NMR, IR, GPC, and MALDI−MS.

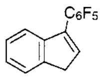
Scheme 1



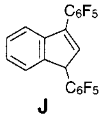
Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all reactions. Decafluorobiphenyl was used as received from Lancaster. Indene (Aldrich) was freshly

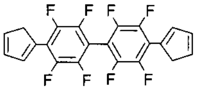
10.1021/ma001424g CCC: $20.00



H



J



K

distilled prior to use and found to be at least 98% pure by ^{1}H NMR analysis. NaH was purchased as a 60% mineral oil dispersion from Aldrich, washed with hexane, dried under vacuum, and stored in a glovebox. NMR experiments were performed using JEOL ECP500 and Varian U400 instruments. THF-d_8 was vapor-transferred from Na/K alloy using a diffusion-pumped vacuum line. ^{19}F NMR spectra were referenced to external C_6F_6 in $CDCl_3$ at −163.00 ppm. $\{^{19}F\}^{13}C$ NMR spectra were particularly useful for resolving signals in the aromatic C−F regions where extensive ^{19}F couplings in the ^{1}H-decoupled spectra prevented us from distinguishing closely spaced signals. C−F coupling constants were approximated from observed splittings. Infrared spectra of were recorded on a Midac M-series instrument operating at 4 cm^{-1} resolution for solid samples, whereas metal carbonyl stretching frequencies of dissolved species were recorded at 1 cm^{-1} resolution. EI mass spectra were obtained using a Fisons VG7070 instrument (direct probe). MALDI−TOF spectra were obtained from matrix-free samples using a Kratos Kompact SEQ spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Room-temperature GPC measurements used a Waters 2690 instrument equipped with viscometric and RI detectors; analytes were eluted with chloroform. GPC measurements at 135 °C were carried out using a Waters 150C instrument equipped with and RI detector; analytes were eluted with 1,2,4-trichlorobenzene; molecular weights are presented in “equivalent polystyrene.”

Polymerization Procedure. A mixture of indene (1.16 g, 10.0 mmol), NaH (1.2 g, 50.0 mmol), and THF (50 mL) was stirred under reflux for about 16 h and then cooled to 25 °C. To the dark purple mixture was added decafluorobiphenyl (3.34 g, 10.0 mmol) in one portion, and the mixture was stirred under reflux for 3 h. The solvent was evaporated thoroughly, and then toluene (50 mL) and water (20 mL) were added with vigorous stirring to hydrolyze the reaction mixture completely. Concentrated aqueous HCl (about 10 mL) was added to acidify the mixture. A gray solid coagulated. The rest of the procedure was carried out under air. The mixture was filtered, and the gray precipitate was washed with toluene and water, collected in a beaker, and dried overnight in a vacuum desiccator charged with anhydrous $CaSO_4$ to afford 100−600 mg of a powdery gray solid that we were not able to identify. The combined biphasic filtrate was separated, and the aqueous layer was extracted with toluene (2 × 20 mL). The combined organic layers were washed with water (2 × 50 mL), dried over $MgSO_4$, filtered, and evaporated to afford a dark brown residue. The residue was triturated with hot hexane (3 × 10 mL), collected on a filter, and dried under vacuum to afford 2.8−3.5 g of a glassy brown solid (**1**). The hexane used to triturate the residue was discarded. Data for the toluene-soluble fraction: IR (KBr) 3078, 3025, 2913, 1645, 1605, 1467, 1275, 971 cm^{-1}; MS (MALDI, 10 signals of highest mass) m/z 3614, 3567, 3185, 3166, 2890, 2775, 2756, 2461, 2365, and 2346; ^{1}H NMR ($CDCl_3$) δ 7.6 (d, end group aromatic CH), 7.4 (br m, end group and repeat-unit aromatic CH), 6.9 (m, end group and repeat-unit vinylic CH), 5.4 (m, repeat-unit sp^3 CH), and 3.7 (m, end group sp^3 CH_2); ^{19}F NMR ($CDCl_3$) δ −37.7 (m, 2 F of end-group), −138.2 (br m, end group and repeat unit), −141.4 (br m, end group and repeat unit), −150.5 (t, end group para CF), −150.7 (t, end group para CF), −160.9 (m, end group CF); much weaker signals were also observed at −128.6, −130.3, −132.4, and −164.0 and were not assigned. Anal. Calcd for $[-C_{21}H_6F_8-]_n$: C, 61.48; H, 1.47. Found: 61.10; H, 1.54.

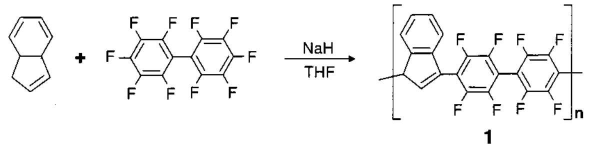
1,3-Bis[4-(pentafluorophenyl)tetrafluorophenyl]indene (2). A mixture of indene (120 mg, 1.0 mmol), NaH (1.2 g, 50 mmol), and THF (100 mL) was stirred under reflux for about 16 h and then cooled. Decafluorobiphenyl (3.3 g, 10 mmol) was added, and the mixture was stirred under reflux for 3 h. The resulting deep red mixture was cooled to 25 °C, and the THF was evaporated. Toluene (100 mL) and water (50 mL) were added, and the mixture was stirred until the hydrolysis was complete. The rest of the procedure was carried out under air. The orange biphasic mixture was separated, and the organic layer was washed with water, dried over $MgSO_4$, filtered, and evaporated to afford a brown oil. The oil was dried for an additional 16 h using a vacuum pump to afford a pale orange solid. The orange solid was transferred to a sublimer, and unreacted decafluorobiphenyl (980 mg) was recovered by fractional sublimation at 80 °C (5×10^{-2} Torr). The remaining orange residue was recrystallized from hexane to afford 360 mg (0.48 mmol, 48%) of a pale tan solid. ^{1}H NMR ($CDCl_3$): δ 7.37 (m, 4 H), 6.84 (s 1 H), 5.33 (s, 1 H). ^{19}F NMR ($CDCl_3$): δ −137.6 (m, 4 F), −138.1 (m, 2 F), −138.4 (m, 4 F), −141.3 (m, 2 F), −150.4 (t, J = 21 Hz, 1 F), −150.6 (t, J = 21 Hz, 1 F), −160.8 (m, 4 F). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 143.3 (CH), 142.6 (C), 138.2 (CH), 130.8 (C), 126.5 (CH), 125.6 (CH), 124.1 (CH), 120.5 (CH), 39.3 (CH_2). $\{^{19}F\}^{13}C$ NMR ($CDCl_3$): δ 144.37 (CF), 144.34 (d, J_{CH} = 1.5 Hz, CF), 106.4 (C); one (C) not observed. MS (EI): 744 (M$^+$). Anal. Calcd for $C_{33}H_6F_{18}$: C, 53.22; H, 0.81. Found: C, 53.22; H, 0.78.

4,4′-Bis(3-indenyl)octafluorobiphenyl (3). A mixture of indene (1.19 g, 10.0 mmol), NaH (2.4 g, 0.10 mol), and THF (100 mL) was stirred under reflux for 16 h and then cooled to 25 °C. Decafluorobiphenyl (334 mg, 1.00 mmol) was added, and the mixture was stirred under reflux for 3 h and then cooled to 25 °C. The solvent was evaporated, and toluene (100 mL) and water (50 mL) were added to hydrolyze the residue. The rest of the procedure was carried out under air. The resulting orange biphasic mixture was separated. The organic layer was washed with water, dried over $MgSO_4$, filtered, and evaporated to afford a dark orange residue. Recrystallization from hexanes and again from chloroform afforded 203 mg (0.37 mmol, 37%) of a pale tan solid. ^{1}H NMR ($CDCl_3$): δ 7.57 (d, ^3J = 7.2 Hz, 2 H), 7.32 (m, 6 H), 6.87 (t, ^3J = 1.9 Hz, 2 H), 3.67 (d, ^3J = 2.2 Hz, 4 H). ^{19}F NMR ($CDCl_3$): δ −138.8 (s, 8 F). ^{19}F NMR (C_6D_6): δ −138.3 (4 F), −138.8 (4 F). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 137.95 (C), 132.32 (C), 127.89 (CH), 126.86 (CH), 123.55 (CH), 121.17 (CH), 45.11 (CH). $\{^{19}F\}^{13}C$ NMR ($CDCl_3$): δ 145.31 (CF), 145.26 (CF), 144.60 (CF), 144.54 (CF), 144.37 (CF), 144.33 (CF), 144.05 (CF), 142.51 (CF), 142.43 (CF), 119.83 (d, $^2J_{CH}$ = 10 Hz, C), 116.73 (C), 105.99 (C), 105.23 (C), 102.37 (C), 102.31 (C). Anal. Calcd for $C_{30}H_{14}F_8$: C, 68.43; H, 2.68. Found C, 67.67; H, 2.56.

Polymer Metalation Experiments. Sodiation (4). Using a small reaction tube interfaced to a high-vacuum line, a mixture of the indene−decafluorobiphenyl polymer (toluene-soluble fraction, 110 mg), sodium hydride (50 mg), and THF-d_8 (about 3 mL) was stirred under argon for 15 h at 25 °C. At first, all the polymer was soluble in the THF. After the reaction was complete, the product mixture contained a significant quantity of sticky, insoluble magenta polymer. An aliquot of the deep magenta mixture was transferred to an NMR tube in a glovebox. Unreacted sodium hydride and the insoluble product fraction were removed from the spectrometer sampling volume by spinning the tube upside-down in a centrifuge for 5 min and then cautiously inverting the tube to decant the clear magenta supernatant containing the polysodiated oligomer (**4**). The ^{1}H NMR spectrum showed signals at 7.38, 7.18, 7.02, 6.84, 6.75, 6.70 (t), 6.62 (t), and 6.30 (d). Similar experiments using the toluene-insoluble polymer fraction also afforded deep magenta reaction mixtures, but none of the species were sufficiently soluble to obtain useful NMR spectra.

$Mn(CO)_3$ Coordination (5). In a 100 mL flask fitted with a condenser and interfaced to a high vacuum line, about 30 mL of THF was condensed into a mixture of the indene-decafluorobiphenylene polymer (toluene-soluble fraction, 410 mg, 0.1 mmol of repeat unit) and sodium hydride (48 mg, 2.0 equiv). The mixture was stirred under argon for 15 h to afford

Scheme 2



a sticky, deep magenta residue. Without removing the solvent, the flask was transferred to a glovebox, where 300 mg (1.1 mmol, 1.1 equiv) of $Mn(CO)_5Br$ was added. The mixture was then stirred under reflux for 15 h, during which time the deep magenta color was replaced by an sticky orange solid. The mixture was cooled, and 20 mL of 10% aqueous ammonium chloride solution was added to coagulate the product. The crude orange product was collected on a filter, then suspended in THF and re-coagulated with 10% aqueous ammonium chloride solution. The coagulated solid was triturated with methanol using a mortar and pestle to obtain 300 mg (55%) of **5** as a fine orange powder. The product was sparingly soluble in chloroform, dichloromethane, and 1,2-dichloroethane but not appreciably soluble in other common organic solvents such as toluene, DMSO, hexanes, or methanol. ^1H NMR ($CDCl_3$): δ 7.65 (br, 2 H), 7.40 (br, 2 H), 5.90 (br m, 1 H). Weak signals arising from unmetalated indenyl groups also appeared at 6.98, 5.38, and 3.71 ppm). ^{19}F NMR ($CDCl_3$): δ −133.6 (br, 4 F), −137.1 (br, 4 F). Weak 4-(pentafluorophenyl)tetrafluorophenyl end group signals (about 5−10% of the total integrated intensity) also appeared at −150.0 and −160.5 ppm. IR (1,2-dichloroethane solution): $\nu_{CO} = 2031, 1957\ cm^{-1}$. Anal. Calcd for $[-C_{24}H_5F_8MnO_3-]_n$: C, 52.58; H, 0.92; Mn, 10.02. Found: C, 52.07; H, 0.77; Mn, 8.59.

Tricarbonyl[η^5-1,3-bis(pentafluorophenyl)indenyl]manganese(I) (6). A solution of $Mn(CO)_5Br$ (82.5 mg, 0.300 mmol) and sodium 1,3-bis(pentafluorophenyl)indenide[5] (155 mg, 0.330 mmol) in THF (15 mL) was stirred under reflux for 40 h and then cooled. The solvent was evaporated, and the residue was recrystallized from pentane/dichloromethane at −20 °C to afford 285 mg (0.243 mmol, 81%) in three crops of tiny crystals. Mp: 202−203 °C. IR (1,2-dichloroethane): $\nu_{CO} = 2030, 1956\ cm^{-1}$. IR (*n*-octane): $\nu_{CO} = 2035, 1967, 1955\ cm^{-1}$. ^1H NMR ($CDCl_3$): δ 7.47 (m, 2 H), 7.32 (m, 2 H), 5.58 (s, 1 H). ^{19}F NMR ($CDCl_3$): δ −134.31 (d, $^3J = 22$ Hz, 4 F), −153.35 (tt, $^3J = 21$ Hz, $^4J = 2$ Hz, 2 F), −160.98 (m, 4 F). Anal. Calcd for $C_{24}H_5F_{10}MnO_3$ C, 49.17; H, 0.86. Found: C, 49.21; H, 0.64.

Results and Discussion

Synthesis. Sodium indenide reacts with 1.0 equiv of decafluorobiphenyl to afford a substantially linear, alternating copolymer (Scheme 2). The polymer is regioregular with respect to substitution at the 1- and 3-positions of indene, and we presume that the relative dispositions of the double bonds in neighboring repeat units is random. The reaction requires 2.0 equiv of a base (NaH) to remove the second and third protons from indene; the third is returned upon workup. NaH was chosen because it does not undergo unwanted side-reactions (such as substitution) with aromatic fluorocarbons. This allowed us to use a large excess of NaH to prepare the sodium indenide and then subsequently add the decafluorobiphenyl in a one-pot procedure. After the reaction was completed, the unreacted sodium hydride was fully quenched by hydrolyzing and acidifying the crude product mixture.

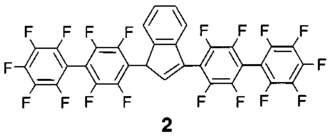
We reasoned that toluene fractionation of the crude polymer at 25 °C into toluene-soluble and toluene-insoluble fractions would provide a substance amenable to solution NMR analysis (see below). The major (typically 90% of the total product weight), toluene-soluble fraction was additionally purified by filtering a dichloromethane solution through a pad of silica gel, whereupon about 90% of its original mass was recovered. Material purified in this way was used for subsequent analyses and reactions. The toluene-insoluble fraction was subsequently found to be insoluble in other common organic solvents as well. The toluene-soluble fraction was also soluble in chloroform, dichloromethane, and THF.

Characterization. The IR spectrum of the soluble fraction showed signals corresponding to all of the expected organic functional groups: aromatic/vinylic C−H (3078, 3025 cm^{-1}), aromatic/olefinic C=C (1640, 1605 cm^{-1}), and C−F (1270). Infrared spectra (as KBr pellets) of the soluble and insoluble fractions were strikingly similar. We speculate that the insoluble fraction either has a higher molecular weight, or it contains enough residual, inextractable soluble polymer to provide an infrared spectrum. An alternative, if spectulative, explanation for the striking insolubility of the minor product component is polymer cross-linking. Although we have tentatively ruled out the pathway **D**−**F** (Scheme 1), other cross-linking mechanisms are possible.

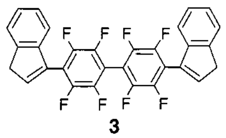
Using the MALDI mass spectrometric technique, we observed ions at *m*/*z* as high as 3614 amu, corresponding to $n = 8$ with two $C_{12}F_9$ end groups. Spectra typically exhibited series of signals that could be assigned to the sum of one to eight repeat units (410 amu, see Scheme 2) plus zero to two fluorine (19 amu) and zero to two indenyl (115 amu) end groups. The toluene-insoluble fraction did not provide useful MALDI−MS spectra.

GPC measurements carried out on the toluene-soluble fraction typically gave $M_n = 3500$ and $M_w = 5700$, suggesting that the average degree of oligomerization is around 10. However, these figures are probably not highly significant, as the prepared polymer chain is much more rigid than the polystyrene molecular weight calibration standards. Small adjustments in reactant ratios and polymerization conditions did not lead to significantly higher molecular weights. A typical GPC trace is shown in Figure 1. Attempts to analyze the toluene-insoluble fraction using GPC, eluting with trichlorobenzene at 135 °C, gave a weak signals with $M_n = 1800$ and $M_w = 4900$, suggesting again that this substance is largely intractable.

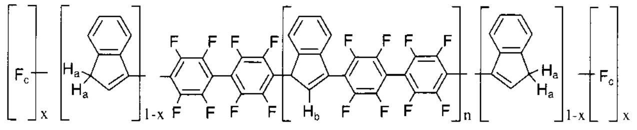
For a generalized linear polymer structure (**1**−**P**) having an arbitrary mole fraction (***x***) of randomly distributed fluoro end groups and a corresponding mole fraction (1 − ***x***) of 3-indenyl end groups, the number-averaged degree of polymerization (***n***) can be determined from the integration of well-resolved features in the ^1H and ^{19}F NMR spectra. 1-Indenyl end groups are not conjugated and can be ruled out. Assignments were based on the NMR spectra of two model compounds (**2** and **3**) that we prepared separately from indene and



2

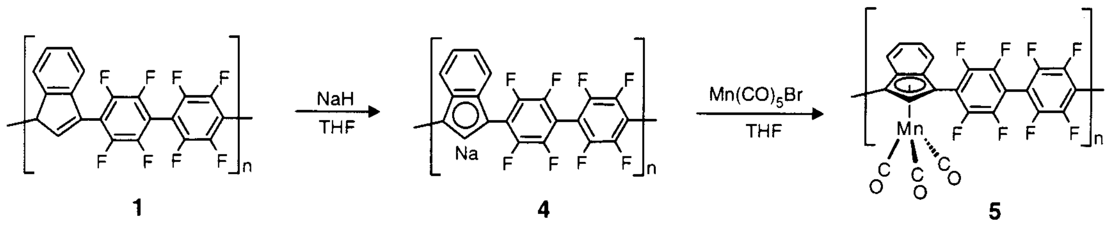


3



1 - P

Scheme 3



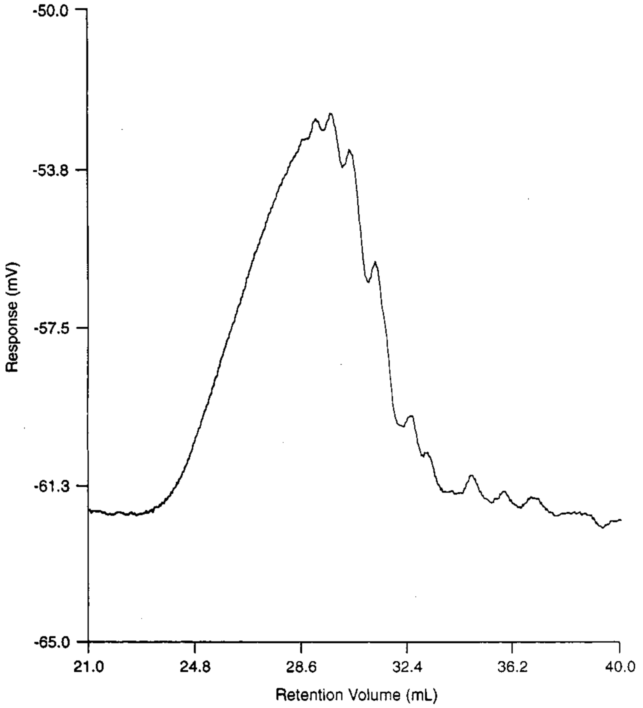


Figure 1. GPC trace (RI chromatogram) of the toluene-soluble polymer fraction (**1**).

decafluorobiphenyl. Each indenyl end group of the polymer (**1**−**P**) has two methylene protons (H_a) at 3.6 ppm in the ^1H NMR spectrum, whereas the methine proton of the repeat unit (H_b) corresponds to the signal at 5.4 ppm. These signals have an intensity ratio that depends on n and x as shown in eq 1 . Similarly, fluoro

$$R_H = \frac{\int H_a}{\int H_b} = \frac{4(1 - x)}{n} \qquad (1)$$

end groups (F_c, corresponding to the single *para* fluorine on each end) are found in a distinct region of the ^{19}F NMR spectrum (−138 to −141 ppm). The ratio of the intensity of F_c to the sum of all the remaining assignable ^{19}F signal intensity (collectively F_d) is given in eq 2.

$$R_F = \frac{\int F_a}{\int F_b} = \frac{x}{4(1 + n)} \qquad (2)$$

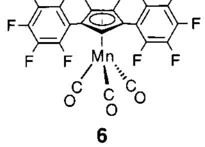
Simultaneous solution of eqs 1 and 2 provides expressions for n and x as a function of one ratio obtained from the ^1H NMR spectrum and one obtained from the ^{19}F NMR spectrum (eqs 3 and 4). Applying eqs 3 and 4 using the toluene-soluble fraction gave a value of $n = 10 \pm 1$. The value of x was typically 0.5−0.9. Small adjustments in the reactant ratio did not lead to significant changes in either x or n.

$$n = \frac{1 - 4R_F}{\frac{R_H}{4} + 4R_F} \qquad (3)$$

$$x = 4R_F \frac{1 + \frac{R_H}{4}}{\frac{R_H}{4} + 4R_F} \qquad (4)$$

Metalation Experiments. Treatment of the toluene-soluble polymer fraction (Scheme 3) with excess NaH in THF-d_8 afforded a deep magenta solution of the polysodiated polymer (**4**). NMR spectroscopic analysis showed that the product of the reaction was the corresponding polymer in which each indene subunit was sodiated. The CH signals arising from the five-membered rings of the end groups (6.22 and 6.87 ppm) and the repeat units (7.06 ppm) were readily assigned using the spectra of pentafluorophenyl-substituted indenyl anions that we reported earlier. Notably, the sodiated polymer (**4**) is much less soluble than its precursor (**1**) in THF, further suggesting that solubility may have impeded chain growth during the preparation of **1**. The toluene-insoluble fraction was also treated with NaH in THF. Although we were not able to analyze the resulting mixture by NMR spectroscopy, we did observe the evolution of hydrogen gas and the formation of the same deep magenta color as we observed starting with the soluble fraction. We did not attempt to isolate the sodiated polymers (**4**).

We are interested in the use of the resulting indenyl anions in the polymer as ligands for transition metals.[8] Indenyl ligands bearing electron-withdrawing substituents offer potential advantages for catalytic applications.[9] We treated the crude sodiated polymer (**4**), comprising both THF-soluble and THF-insoluble material, with $Mn(CO)_5Br$ in THF at 65 °C for 24 h (Scheme 3). After an aqueous ammonium chloride workup, we obtained a yellow solid having NMR spectra consistent with the $Mn(CO)_3$-functionalized polymer (**5**). Infrared spectra in 1,2-dichloroethane solution showed carbonyl stretching bands at 2031 and 1957 cm^{-1} corresponding to symmetric and asymmetric normal modes under approximate C_{3v} symmetry. The infrared spectrum of a well-defined model compound (**6**) showed corresponding



6

signals at 2030 and 1956 cm^{-1}. The ^1H NMR spectrum of **5** showed greatly attenuated signals corresponding to sp^3 C−H units along the polymer chain. Microanalysis for manganese corresponded to about 85% of the stoichiometric amount. These data suggest that most of the indenyl units of **1** were $Mn(CO)_3$−functionalized by this two-step (one-pot) procedure, even though only a slight (10 mol %) excess of $Mn(CO)_5Br$ was used.

Conclusions

A new 1,3-polymerization mode for indene is demonstrated in a step−growth nucleophilic aromatic substitution polymerization of indene and decafluorobiphenyl. The product is readily separated into a well-characterized, toluene-soluble fraction with a number-averaged decameric degree of polymerization, and a largely intractable insoluble fraction. The polymer is readily metalated with $Mn(CO)_3$ fragments to obtain an organometallic polymer. Work is underway in our laboratories to improve the solubility of these polymers using alkyl-substituted indenes. An improvement in solubility should enable us to pursue higher molecular weights. We are also investigating the reaction of indenyl anions with other perfluoroarenes.

Acknowledgment. We thank K. Harich for carrying out the MALDI analyses, Y. Kim and J. Gunderson for carrying out the GPC analyses, and T. Glass for assistance with the NMR measurements. Funding was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Virginia Tech Chemistry Department.

References and Notes

(1) Undergraduate research participant.

(2) (a) Givehchi, M.; Tardi, M.; Polton, A.; Sigwalt, P. *Macromolecules* **2000**, *33*, 710. (b) Thomas, L.; Polton, A.; Tardi, M.; Sigwalt, P. *Macromolecules* **1995**, *28*, 2105. (c) Kennedy, J. P. *J. Polym. Sci. Part A, Polym. Chem.* **1999**, *37*, 2285.

(3) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.

(4) Stradiotto, M.; Hazendonk, P.; Bain, A. D.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **2000**, *19*, 590.

(5) Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 327.

(6) Hollandsworth, C. B.; Hollis, W. G.; Slebodnick, C.; Deck, P. A. *Organometallics* **1999**, *18*, 3610.

(7) (a) Irvin, J. A.; Neef, C. J.; Kane, K. M.; Cassidy, P. E.; Tullos, G.; St. Clair, A. K. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 1675. (b) Gerbi, D. J.; Dimotsis, G.; Morgan, J. L.; Williams, R. F.; Kellman, R. *J. Polym. Sci. Polym. Lett.* **1985**, *23*, 551. (c) Farnham, A. G.; Johnson, R. N. **1967**, U. S. Pat. 3,332,909 (to Union Carbide Corp.).

(8) (a) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (b) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123. (c) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602−1621. (d) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. (e) Plenio, H.; Hermann, J.; Leukel, J. *Eur. J. Inorg. Chem.* **1998**, *12*, 2063. (f) Heo, R. W.; Somoza, F. B.; Randall, T. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (g) Southard, G. E.; Curtis, M. D. *Organometallics* **1997**, *16*, 5618.

(9) Brinkman, J. A.; Nguyen, T. T.; Sowa, J. R. *Org. Lett.* **2000**, *2*, 981.

MA001424G