Hyperbranched Poly(4-Acetylstyrene) by Ruthenium-Catalyzed Step-Growth Polymerization of 4-Acetylstyrene

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ABSTRACT: Treatment of 4-acetylstyrene (an AB_2 monomer) with dihydridocarbonyltris(triphenylphosphine)ruthenium leads to hyperbranched poly(4-acetylstyrene) whose structure has been determined by ^1H and ^{13}C NMR spectroscopy. The hyperbranched material has been characterized by GPC, IR, UV, TGA, DSC, and elemental analysis. Polymerization occurs by Ru-catalyzed addition of C−H bonds which are adjacent to the activating acetyl group across the C−C double bond of the vinyl group in both a Markovnikov and an anti-Markovnikov manner.

Introduction

Highly branched macromolecules have attracted considerable interest due to their unique properties and potential applications.[1−4] These can be divided into two major subgroups: dendrimers and hyperbranched materials. Dendrimers are macromolecules which have a regular and controlled pattern of branching. In general, they have been prepared by multistep sequential synthesis. On the other hand, hyperbranched materials can be prepared in a single step by the direct polymerization of a monomer which has two mutually reactive functional groups A and B, present in a ratio of AB_x where x is greater than or equal to 2. Compared to dendrimers, hyperbranched materials do not have a well-defined architectural structure, but rather an irregular pattern of branching. Despite these differences, chemically related dendrimers and hyperbranched materials often have similar properties.

At this time, there are only a few examples of transition metal catalyzed reactions which have been utilized to prepare hyperbranched materials. Among these are the tetrakis(triphenylphosphine)palladium(0)-catalyzed, Suzuki, polymerization of (3,5-dibromophenyl)-boronic acid which yields hyperbranched polyphenylene[4,5] and the palladium(0)-catalyzed coupling of aryl bromides or iodides with terminal acetylenes, the Sonogashira procedure, which gives poly (phenylacetylene) dendridic macromolecules.[6,7] We should like to report a novel Ru-catalyzed step-growth reaction which leads to hyperbranched materials.

We have previously shown that acetophenone undergoes Ru catalyzed step-growth copolymerization with certain α,ω-dienes.[8−11] This reaction was initially reported in monomer systems by Murai, who found that dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) catalyzes the *ortho* alkylation reaction of acetophenone with vinylsilanes.[12−14] In similar polymerization reactions between acetophenone and α,ω-divinylsilanes, acetophenone serves as a difunctional monomer since the acetyl group activates both of the *ortho* C−H bonds. On the basis of this analysis, 4-acetylstyrene should be a suitable AB_2 monomer for the synthesis of hyperbranched materials. In fact, treatment of 4-acetylstyrene with activated Ru catalyst[12] in toluene at 70−100 °C for 24 h, or at 135 °C for 35 h, or directly with $[Ph_3P]_3RuH_2CO$ catalyst without solvent at 85−125 °C for 4 h leads to hyperbranched poly(4-acetylstyrene). The materials are spectroscopically very similar and are different from linear poly(4-acetylstryene), prepared by free radical polymerization of 4-acetylstyrene.

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Experimental Section

^1H and ^{13}C NMR spectra were obtained on a Bruker AC-250 spectrometer operating in the FT mode. Five percent w/v solutions in chloroform-*d* were used to obtain ^1H NMR spectra. Fifty percent w/v solutions in chloroform-*d* were used to obtain ^{13}C NMR spectra. Residual chloroform was used as an internal standard for ^1H NMR spectra. ^{13}C NMR spectra were run with both broad band proton decoupling and with off resonance proton decoupling. The multiplicity observed in the off resonance ^{13}C NMR spectra permit the determination of the number of protons bonded to each particular carbon. IR spectra of neat films on NaCl plates were recorded on an IBM FT IR spectrometer. UV spectra of THF solutions were recorded on a Shimadzu UV-260 ultraviolet visible spectrometer.

GPC analysis of the molecular weight distribution of the hyperbranched polymeric materials was performed on a Waters system composed of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector and a model 820 Maxima control system. A linear Waters Styragel HR5E 7.8 mm × 30 cm column packed with <5 μm particles of monodisperse cross-linked styrene divinylbenzene copolymer was used for the analysis. HPLC grade THF was used as the eluting solvent at a flow rate of 0.8 mL/min. The retention time was calibrated against those of known monodisperse polystyrene standards: M_w 929 000; 114 200, 47 500, 18 700, and 2200 whose M_w/M_n are less than 1.09.

TGA of the polymers was measured on a Shimadzu TGA-50 instrument. The temperature program for the analysis was 50 °C for 1 h followed by an increase of 3 °C/min to 800 °C with a nitrogen flow of 30 mL/min.

The T_g of the polymer was determined by DSC on a Perkin-Elmer DSC-7. The mp of indium (156 °C) was used to calibrate the DSC. The program of the analysis was 25 °C for 10 min followed by an increase in temperature of 10 °C/min to 150 °C.

4-Acetylstyrene. 2-Phenylethyl chloride (Aldrich) (14.2 g, 0.1 mol), acetyl chloride (16 g, 0.2 mol), and aluminum chloride (15 g, 1.1 mol) were reacted in ethylene dichloride to give 2-(*p*-acetylphenyl)ethyl chloride (14 g, 77 mmol), 77% yield. 2-*p*-(Acetylphenyl)ethyl chloride was dehydrohalogenated by steam distillation from a two to one mixture of triethanolamine and water,[15] to give 4-acetylstyrene, 8.4 g, 58 mmol, 75% yield, mp 33−34 °C, lit. mp 33 °C.[16] ^1H NMR, δ: 2.58 (s, 3H), 5.38 (d, 1H, J = 11 Hz) 5.86 (d, 1H, J = 17.5 Hz), 6.74 (dd, 1H, J =

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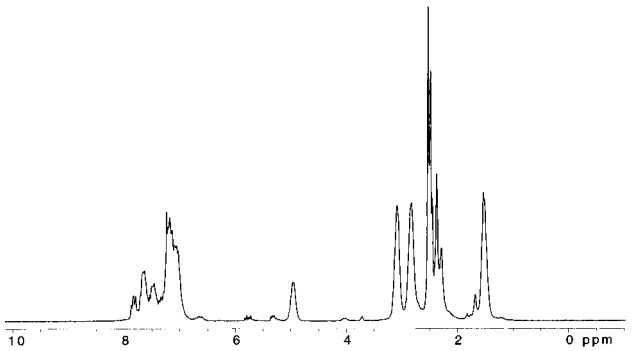


Figure 1. ^{1}H NMR spectrum of hyperbranched poly(4-acetylstyrene) (A).

17.5 and 10 Hz), 7.47 (d, 1H, J = 8 Hz), and 7.91 (d, 1H, J = 8 Hz). The ^{1}H NMR and IR spectra were in agreement with those previously reported[17]

Free Radical Polymerization of 4-Acetylstyrene. Linear Poly(4-Acetylstyrene). 4-Acetylstyrene (5 g, 34 mmol) was placed in a 10 mL round bottom flask with benzoyl peroxide (25 mg, 2 mmol). The flask and its contents were heated to 90 °C for 1 h. The polymer was soluble in THF and was purified by precipitation from methanol. M_w/M_n = 322 000/142 000. Its ^{1}H NMR spectrum was in complete agreement with those previously reported.[18,19]

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) was prepared from ruthenium trichloride trihydrate.[20]

Hyperbranched Poly(4-acetylstyrene). In an Ace pressure tube equipped with a threaded Teflon seal was placed Ru (55 mg, 0.06 mmol), styrene (6.9 μL, and 3 mL of toluene. The tube and its contents were purged with argon three times, sealed, and heated at 135 °C for 3 min. This process "activates" the Ru catalyst. The tube and its contents were cooled and opened under argon, and 4-acetylstyrene (800 mg, 5.5 mmol) was added. The tube was resealed. The temperature was increased from 70 to 100 °C over 24 h (A) or the temperature was held constant at 135 °C for 35 h (B). Finally, the polymerization was conducted **without** activation of the Ru catalyst and without solvent (C). In this case, Ru (130 mg, 0.14 mmol) and 4-acetylstyrene (980 mg, 6.7 mmol) were directly combined and were heated at 135 °C for 4 h (C). Methanol was added to precipitate the product. Volatile solvents were removed by decantation. The residue was taken up in a minimum amount of THF, and the product was precipitated by addition of methanol. This process was repeated five times. In this way, 700 mg, an 88% yield, was obtained. Similar yields were obtained under conditions B and C. The hyperbranched material was insoluble in methanol, ethanol, and cyclohexane but was soluble in THF and toluene. In three separate experiments under conditions A, hyperbranched materials with M_w/M_n = 4160/3580, 3710/3290, and 3700/3280 were obtained. Under conditions B, material with M_w/M_n = 5730/4620 was obtained. Finally, under conditions C hyperbranched material with M_w/M_n = 13 900/10 600 was secured. The spectral properties of hyperbranched poly(4-acetylstyrene) prepared under conditions A, B, or C are quite similar. Differences in intensities of certain signals in the ^{1}H and ^{13}C NMR of hyperbranched poly(4-acetylstyrene) prepared under conditions A, B or C are discussed in the Results and Discussion. The spectral data presented here are for hyperbranched poly(4-acetylstyrene) prepared under conditions A. ^{1}H NMR, δ: 7.8 (dd, J = 10 Hz), 7.67 (br m), 7.51 (br m), 7.3−7.0 (br m) (integration of the four preceding peaks is 6.53), 6.70 (d, J = 10 Hz), 6.62 (d, J = 10 Hz), 5.81 (d, J = 7.5 Hz), 5.74 (d, J = 7.5 Hz), 5.35 (d, 5 Hz), 5.31 (d, J = 5 Hz) (integration of the six preceding peaks is ~0.24), 4.96 (br s, 0.65), 3.10 (br s, 2.00), 2.86 (br s, 2.00), 2.55 (s), 2.51 (s), 2.47 (s), 2.39 (s), 2.30 (s) (integration of the five preceding peaks is 5.47), 1.68 (s, 0.24), 1.54 (d, 2.25, J = 4.5 Hz). For the ^{1}H NMR spectrum see Figure 1. ^{13}C NMR, δ: 208.0, 202.0, 200.4, 197.1, 152.3, 150.7, 146.6, 146.0, 144.6, 142.0, 135.8, 134.6, 131.9, 131.3, 130.3, 129.0, 128.9, 128.0, 126.4, 126.2, 125.3, 39.3, 37.9, 36.4, 30.0, 29.4, 26.5, 21.8; (off resonance) 21.8 (q), 26.5 (q), 29.4 (q), 30.0 (q), 36.4 (t), 37.9 (t), 39.3 (d). IR, ν: 2971, 2932, 1679, 1653, 1606, 1561, 1457, 1437, 1414, 1357, 1252, 961, 910, 828, 735 cm^{-1}. UV, λ (ϵ): 222 (1.18 × 10^4), 245 (9730), 249 (1.11 × 10^4), 255 (1.13 × 10^4), 259 nm (9.43 × 10^3). T_g = 120 °C. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 80.79; H, 6.84.

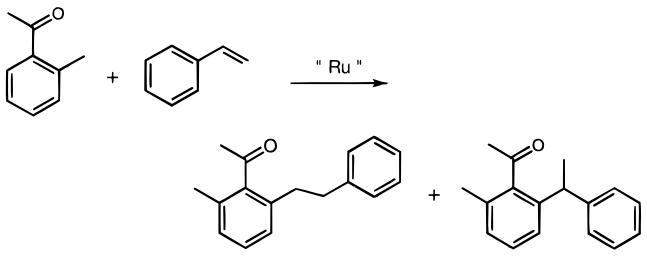
Results and Discussion

4-Acetylstyrene is a suitable monomer for Ru-catalyzed step-growth hyperbranched polymerization in that it contains two reactive C−H bonds which are *ortho* to the activating carbonyl group but only a single reactive terminal vinyl group. Unfortunately, 4-acetylstyrene cannot be prepared by Friedel-Crafts acylation of styrene. This is due to the fact that the HX produced in this reaction causes the rapid acid catalyzed polymerization of styrene. 4-Acetylstyrene has been produced indirectly by a two-step procedure. Friedel-Crafts acetylation of 2-phenylethyl chloride gives 2-(*p*-acetylphenyl)-ethyl chloride which undergoes dehydrohalogenation on steam distillation from triethanolamine and water.[15] Thermal free radical polymerization of 4-acetylstyrene catalyzed by benzoyl peroxide yields linear poly(4-acetylstyrene).

We have carried out hyperbranched polymerization of 4-acetylstyrene with a Ru catalyst which has been activated by previous treatment with a stoichiometric amount of styrene at 135 °C. Hydrogenation of styrene by $[Ph_3P]_3RuH_2CO$ gives ethylbenzene and results in quantitative lost of hydrogen from the Ru complex. This generates a coordinately unsaturation Ru catalyst (A and B).[11] After 3 min, the catalyst was cooled and 4-acetylstyrene was added. Alternatively, we have directly combined 4-acetylstyrene with $[Ph_3P]_3RuH_2CO$ (conditions C). In this case, we believe that a stoichiometric amount of 4-acetylstyrene is reduced to 4-ethylacetophenone. Thermal free radical polymerization of 4-acetylstyrene is not a problem under these conditions.

The molecular weight distribution of the hyperbranched material prepared under conditions A, based on GPC comparison to linear PS standards, is rather low but reproducible in three separate experiments. Hyperbranched material prepared from an AB_2 type monomer has only a single A group in each macromolecule. Integration of the ^{1}H NMR of the terminal vinyl protons (−HC=CH_2) (6.70−5.31 ppm) compared to the (−CH_2−CH_2−) and (−CH−CH_3) protons permits independent determination of M_n ~ 3600 in close agreement with those obtained by GPC. The molecular weight by GPC of the hyperbranched materials prepared under conditions B and C is higher. No signals in the ^{1}H NMR due to terminal vinyl groups are observed in materials prepared under either conditions B or C. Therefore, in these experiments we have no independent calibration of the GPC M_w/M_n value obtained. It is often the case that molecular weights by GPC of hyperbranched materials are low.[21]

The structure of the hyperbranched poly(4-acetylstyrene) can be deduced from the ^{1}H, ^{13}C, and off resonance ^{13}C NMR spectra. While anti-Markovnikov regioselectivity is observed in the Ru-catalyzed addition of the *ortho* C−H bonds of acetophenone across the C−C double bond of vinyl silanes, Murai has previously reported that the Ru-catalyzed reaction between 2-methylacetophenone and styrene yields both 2-methyl-6-(2-phenyl-1-ethyl)acetophenone (59%) and 2-methyl-6-(1-phenyl-1-ethyl)acetophenone (14%).[14]

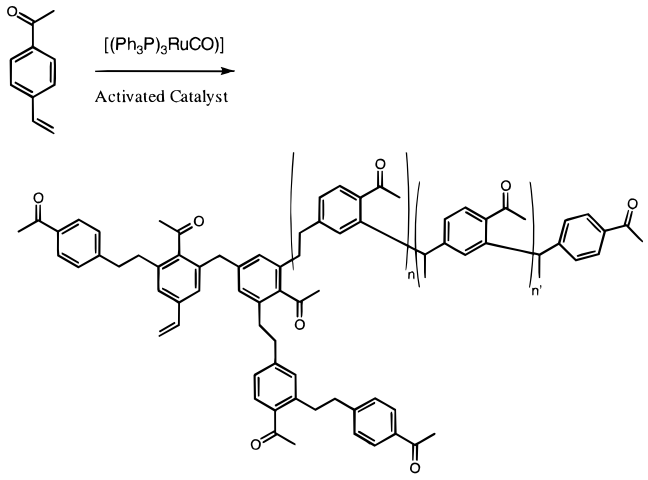


Similar structures have been observed in the spectra of hyperbranched poly(4-acetylstyrene). Thus ($-CH_2-CH_2-$) units give rise to two peaks of equal intensity at 2.86 and 3.10 ppm in the ^1H NMR spectra as well as signals at 36.4 (triplet) and 37.9 (triplet) ppm in the off resonance ^{13}C NMR. On the other hand, ($-CH-CH_3$) units give rise to signals at 4.96 and 1.54 ppm (relative intensity one to three) in the ^1H NMR as well as to resonances at 21.8 (quartet) and 39.3 (doublet) ppm in the off resonance ^{13}C NMR. The ratio of these two types of units, determined by integration of the respective ^1H NMR signals ($-CH_2-CH_2-$)/($-CH-CH_3$), depends on polymerization conditions. A 1:1 ratio is found for hyperbranched poly(4-acetylstyrene) prepared under conditions A, a 2:1 ratio under conditions B and finally a 1:1.5 under conditions C. In all cases, the percentage of ($-CH-CH_3$) units is significantly higher than found by Murai.

Three resonances are observed at 26.5, 29.4, and 30.0 ppm in the ^{13}C NMR. In the off resonance ^{13}C NMR these are quartets and have been assigned to three distinct methyl carbons of the acetyl groups, whereas four resonances due to carbonyl carbons of the acetyl groups are detected in the ^{13}C NMR at 208.1, 202.1, 200.4, and 197.0 ppm. These can be assigned on the basis of ^{13}C NMR of C=O carbons of model monomeric compounds and polymers: 4-methylacetophenone (196.2 ppm), 2,4-dimethylacetophenone (199.2 ppm), 2,4,6-trimethylacetophenone (206.6 ppm), and poly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-1,3-phenylene) (208.1 ppm).[22] We believe the resonance at 197.1 ppm in the ^{13}C NMR spectrum of hyperbranched poly(4-acetylstyrene) results from C=O carbons which have no *ortho* alkyl groups, those at 200.4, and 202.0 ppm are due to C=O carbons which have one *ortho* alkyl group, and finally the signal 208.1 ppm is assigned to C=O carbons which have two *ortho* alkyl groups. Note there are two types of alkyl groups ($-CH_2-CH_2-$) and ($-CH-CH_3$).

Comparison of the integrations of the ^1H NMR signals and the ^{13}C NMR due to C=O carbons is consistent with the following detailed assignments. The signals at 200.4 ppm is due to a C=O carbon which has a ($-CH_2-CH_2-$) group adjacent to it, while that at 202.0 ppm is assigned to a C=O carbon which has a ($-CH-CH_3$) group next to it. The signal at 208 ppm is quite broad. This may result from overlap of three ^{13}C NMR signals: one may be due to a C=O carbon which has two ($-CH_2-CH_2-$) groups adjacent to it, one to a C=O carbon which has a ($-CH_2-CH_2-$) and a ($-CH-CH_3$) adjacent to it, and finally one to a C=O carbon which has two ($-CH-CH_3$) groups next to it.

Integration of the ^{13}C NMR C=O signals of material prepared under conditions C (C) indicates that there are 5% terminal units, 88% of the units have a single *ortho* alkyl group (linear), and finally ~7% of the units which have two *ortho* alkyl groups (branched). Under conditions A, the material is 4% branched, 87% of the units have a single *ortho* alkyl group, and 9% of the groups are terminal units. The major difference between hyperbranched (4-acetylstyrene) A and C is the degree of branching.



The high molecular weight hyperbranched poly(4-acetylstryene) is obtained under conditions C because 4-acetylstyrene is a trifunctional molecule. Thus stoichiometric reaction of 4-acetylstyrene with 2% $[Ph_3P]_3RuH_2CO$ will yield 2% 4-ethylacetophenone and the active coordinately unsaturated catalyst $[Ph_3P]_3RuCO$. 4-Ethylacetophenone is still a difunctional monomer since it has two reactive *ortho* C−H bonds. It can be incorporated into the hyperbranched polymer as a linear unit. For this reason, in the case of 4-acetylstyrene *in-situ* catalyst activation does not result in termination and low molecular weights. In fact, the necessity to open the system after catalyst activation (A and B) apparently adversely affects the polymerization.

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