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Ruthenium catalyzed copolymerization of 2-acetylphenanthrene and α,ω-dienes

Direct synthesis of copolymers which regularly incorporate 2-aceto-1,3-phenanthrenylene units

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Summary

Copolymers with 2-aceto-1,3-phenanthrenylene units in the chain have been directly prepared by Ru catalyzed step-growth copolymerization of 2-acetyl phenanthrene and α,ω-dienes such as 1,3-divinyltetramethyldisiloxane. Copolymers which incorporate 2-aceto-1,3-phenanthrenylene units possess higher T_gs and increased thermal stability compared to analogous copolymers which have 2-aceto-5-phenyl-1,3- phenylene(biphenyl) or 2-aceto-1,3-phenylene units. Fluorescence spectra of these copolymers have been obtained.

Introduction

Polymers which incorporate phenanthrene as a pendant substituent or terminal group as well as polymers with the phenanthrene nucleus in the main polymer chain have been recently prepared. For example, anionic polymerization of methyl methacrylate initiated with 1-(9-phenanthryl)-1-phenyl-*n*-hexyllithium, formed by addition of *n*-butyllithium to 1-(9-phenanthryl)-1-phenylethylene, yields PMMA which incorporates a phenanthrene chromophore at the end of each polymer chain [1]. Likewise, reaction of polystyryllithium with 1-(9-phenanthryl)-1-phenylethylene results in polystyrene (PS) which has a phenanthrene chromophore attached to the end of each PS chain [2]. This was confirmed by the good agreement of M_n(GPC) and M_n(UV). On the other hand, PS in which each chain is randomly labeled with a number of phenanthrene units has been produced by photolysis of a benzene solution of PS and 9-bromophenanthrene [3]. Spectroscopic properties of such phenanthrene labeled polymer chains can be studied either by absorption or fluorescence spectroscopy.

Polymers which regularly incorporate phenanthrene in the polymer chain have been prepared by chemical transformation of polymers which have aromatic groups in their backbones. There is considerable interest in modification of existing polymers [4,5]. For example, poly(1,3-arylene vinylenes) in which the vinyl carbons are substituted with electron rich aryl groups undergo oxidative cyclization with $FeCl_3$ to yield poly(10-aryl-2,9-phenanthrenylenes) [6]. Copoly-(4,4'-*cis*-stilbene/ethylene), formed by ring opening metathesis polymerization (ROMP) of [2,2]paracyclophan-1-ene with a Schrock Mo catalyst, undergoes quantitative oxidative photocyclization in benzene solution in the presence of a stoichiometric amount of I_2 and an excess of propylene oxide to yield copoly

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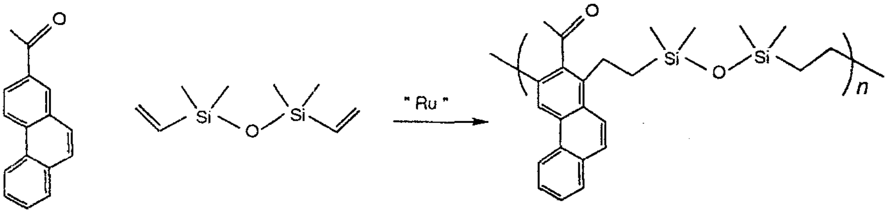
(3,6-phenanthrenylene/ethylene) [7]. 2,2'-Dibenzoylbiphenyl units present in poly(arylene ether)s can be converted into 9,10-diaryl phenanthrene units by use of Lawesson's reagent [8, 9]. The incorporation of phenanthrene nuclei in these polymers results in increased crystallinity, T_g, resistance to solvents, as well as uv absorption and fluorescence.

We should like to report a novel method to regularly incorporate directly phenanthrene nuclei into polymer backbones. 2-Acetylphenanthrene undergoes Ru catalyzed copolymerization with α,ω-dienes such as 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl- 3,6-disila-1,7-octadiene to yield regular copolymers in which 2-aceto-1,3-phenanthrenylene units are part of in the polymer backbone.



We have previously been successful in carrying out ruthenium catalyzed copolymerizations between acetophenone and α,ω-dienes [10-14].

Experimental:

^1H and ^{13}C NMR spectra were obtained on a Bruker AC-250 spectrometer operating in the Fourier Transform mode. ^{29}Si NMR were recorded on an IBM-Bruker WP-270-SY spectrometer. Five percent w/v solutions in chloroform-*d* were used to obtain NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. ^{29}Si NMR spectra, referenced to TMS, were obtained using a gated decoupling pulse sequence (NONOE) with a 20 sec delay [15]. Chloroform was used an internal standard for ^1H and ^{13}C NMR spectra. IR spectra of neat films on NaCl plates were recorded on an IBM FT IR spectrometer. UV spectra of cyclohexane solutions were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer. Fluorescence spectra of cyclohexane solutions were recorded on a Perkin Elmer Luminescence spectrometer LS-5. The wavelength of the excitation energy was 260 nm

GPC analysis of the molecular weight distribution of the copolymers was performed on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector and a model 820 Maxima control system. A series of three 7.8 mm x 30 cm columns packed with <10 μm particles of monodisperse crosslinked styrene divinylbenzene copolymer were used: 1 x 10^4 A° (Waters Ultrastyragel), 1 x 10^3 A°(Waters Ultrastyragel) and 500 A° (Polymer Laboratories Plgel). HPLC grade THF was used as the eluting solvent at a flow rate of 1 mL/min. The retention times were calibrated against polystyrene standards: M_w 612,000; 114,200; 47,500; 18,700; 5,120; 2,200 M_w/M_n < 1.09.

TGA analysis of the polymers was carried out on a Perkin-Elmer TGA-7 instrument with a nitrogen flow rate of 40 cc/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C/min to 750°C. The T_gs of the copolymers were determined by DSC on a Perkin-Elmer DSC-7 instrument. The melting points of indium (156°C) and water (0°C) were used to calibrate the DSC. The program of the analysis was -70°C for 10 min followed by an increase in temperature of 10°C/min to 150°C.

Elemental analysis - Oneida Research Services, Whitesboro, NY.

All reactions were conducted in flame dried equipment under argon. 1,3-Divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene were obtained from United Chemical Technologies. Dihydridocarbonyl *tris*(triphenylphosphine)ruthenium (Ru) was prepared from ruthenium trichloride [16]. 2-Acetylphenanthrene and 4-acetylbiphenyl were purchased from Aldrich.

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-phenyl-1,3-phenylene)(I)

4-Acetylbiphenyl (0.59 g, 3.0 mmol), 1,3-divinyltetramethyldisiloxane (0.56 g, 3.0 mmol), xylene (2 mL), Ru (0.07 g, 0.076 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube (15 mL, 10.2 cm long). The tube and its contents was sealed with a Teflon bushing and an FETFE "O" ring under argon. The reaction mixture was stirred at 150°C for 24 h. The color of the reaction mixture changed from colorless to black. Pentane (5 mL) was added and the mixture was stirred for several min to extract the polymer. This process was repeated. The pentane was removed from the crude polymer by evaporation. The copolymer was purified by three precipitations from THF/methanol. 0.92 g, 80% yield of pure copolymer, M_w/M_n = 17,390/9,930, Tg = 2.5°C, was obtained. ^{1}H NMR δ: 0.11(s, 12H), 0.90(m, 4H), 2.49(s, 3H), 2.56 (m, 4H), 7.26-7.40(m, 5H), 7.54(d, 2H, J = 10 Hz). ^{13}C NMR δ: 0.24, 20.92, 26.85 33.10, 124.94, 127.12, 127.36, 128.67, 139.88, 140.31, 140.86, 141.75, 208.04. ^{29}Si NMR δ: 7.28. IR ν: 2956, 1965, 1697, 1601, 1500, 1412, 1353, 1254, 1179, 1057, 840, 797, 697 cm^{-1}. UV λ, nm(ε): 256 (18,180), 258 (17,830). Elemental Anal. Calcd for $C_{22}H_{30}O_2Si_2$: C, 69.11; H, 7.85. Found: C, 68.40; H, 7.49.

Copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-phenyl-1,3-phenylene) (II).

4-Acetylbiphenyl (0.59 g, 3.0 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.59 g, 3.0 mmol), xylene (2 mL), Ru (0.07 g, 0.076 mmol) and a Teflon covered magnetic stirring bar were placed in a pressure tube as above. In this way, 0.85 g, 72% yield of II, M_w/M_n = 11,000/ 5900, Tg = 11 °C was obtained. ^{1}H NMR δ: -0.03(s, 12H), 0.42(s, 4H), 0.84-0.90 (m, 4H), 2.49(s, 3H), 2.55(m, 4H), 7.27 (s, 2H), 7.43(m, 3H), 7.58(d, 2H, J = 10 Hz). ^{13}C NMR δ: -4.16, 6.97, 17.54, 27.48, 33.11, 124.92, 127.14, 127.36, 128.67 139.77, 140.60, 140.91, 141.73, 208.08. ^{29}Si NMR δ: 4.27. IR ν: 3033, 2952, 2902, 1697, 1599, 1558, 1500, 1411, 1353, 1248, 1177, 1134, 1083, 1054, 831, 697 cm^{-1}. UV λ, nm(ε): 259 (16,600), 271 (16,500) Elemental Anal. Calcd for $C_{24}H_{34}OSi_2$: C, 73.10; H, 8.63. Found: C, 72.28; H, 8.14.

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-1,3-phenanthrenylene (III).

Ru (0.07 g, 0.076 mmol), xylene (2 mL), styrene (7.8 μL, 0.076 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube. The tube and its contents were heated at 120°C for 3 min. 2-Acetylphenanthrene (0.66 g, 3.0 mmol), and 1,3-divinyltetramethyldisiloxane (0.56 g, 3 mmol) were added to the pressure tube which was sealed. The reaction was then carried out and worked up as above. In this way, 0.82 g, 67% yield of III, M_w/M_n = 64500/

51,170, T_g = 46°C was obtained. ^{1}H NMR δ: 0.21-0.31(m, 12H), 1.03-1.13(m, 4H), 2.58(s, 3H), 2.74-2.83(m, 2H), 2.97(m, 2H), 7.52-7,90 (m, 5H), 8.44-8.64 (m, 2H). ^{13}C NMR δ: 0.36, 20.84, 21.41, 23.20, 24.03, 27.41, 33.36, 120.34, 122.14, 122.83 123.19 125.34, 126.62, 127.23, 127.70, 128.37, 130.24, 130.82, 131.72, 136.24 137.58, 208.34. ^{29}Si NMR δ: 7.41. IR ν: 2957, 1694, 1413, 1256, 1058, 841 cm^{-1}. UV λ, nm(ε): 261(61,600), 280(23,000), 293(17,000), 305 (15,600), 336(1,720), 354(1,550). Elemental Anal. Calcd for $C_{24}H_{30}O_2Si_2$: C, 70.94; H, 7.39. Found: C, 70.35; H, 6.99.

Copoly(3,3,6,6-tetramethyl-3,6-disila-1,7-octanylene/2-aceto-1,3-phenanthrenylene (IV)

Ru (0.07 g, 0.076 mmol) was activated as above. 2-Acetylphenanthrene (0.66 g, 3.0 mmol) and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.59 g, 3.0 mmol) were then added to the pressure tube. The reaction was carried out and worked up as above. In this way, 1.1 g, 82% of IV M_w/M_n = 71,000/ 53,000, T_g = 56°C was obtained. ^{1}H NMR δ: 0.08-0.20(m, 12H), 0.52-0.62(m, 4H), 1.02 (m, 4H), 2.60(s, 3H), 2.73-2.77(m, 2H), 3.09-3.26(m, 2H), 7.54-7.85(m, 5H), 8.47(s, 1H) 8.68-8.71(m, 1H). ^{13}C NMR δ: -4.00, 7.14, 18.08, 24.70, 28.10, 33.40, 120.35, 122.18, 122.88, 123.25, 125.39, 126.67, 127.27, 128.42, 130.31, 130.85 131.77, 136.52, 137.94, 139.97, 208.34. ^{29}Si NMR δ: 4.37. IR ν: 2953, 2901, 1698, 1417, 1355, 1279, 1248, 1176, 1133, 1077, 1055, 913, 903, 831, 746, 727, 650 cm^{-1}. UV λ, nm(ε): 263 (28,500), 281 (9,720), 293 (7,250), 305 (6,530). Elemental Anal. Calcd for $C_{26}H_{34}OSi_2$: C, 74.64; H, 8.15. Found: C, 74.80; H, 8.08.

Results and Discussion:

High molecular weight copolymers which regularly incorporate 2-aceto-1,3-phenanthrenylene units have been prepared by the activated [12] Ru catalyzed step-growth copolymerization of 2-acetylphenanthrene and α,ω-dienes such as 1,3-divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6- disila-1,7-octadiene. Lower molecular weight copolymers have been prepared by reaction of 4-acetylbiphenyl with α,ω-dienes with unactivated Ru catalyst. Attempts to carry out similar copolymerization between 2-acetylnaphthalene and α,ω-dienes were unsuccessful. This major difference in reactivity is not understood.

As expected, such polymers have significantly higher T_g's than the corresponding polymer which incorporate 2-aceto-1,3-phenylene or 2-aceto-5-phenyl-1,3- phenylene units (Table 1).

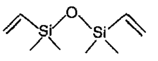
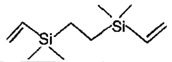
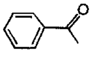
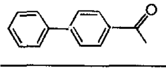
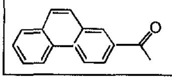
Monomers		
	-33.2°C	-17.1°C
	3.9°C	7.83°C
	45.3°C	53.6°C

Table 1. The Glass Transition Temperature of Copolymers.

Fluorescence spectra of these polymers have been obtained (Figure 1).

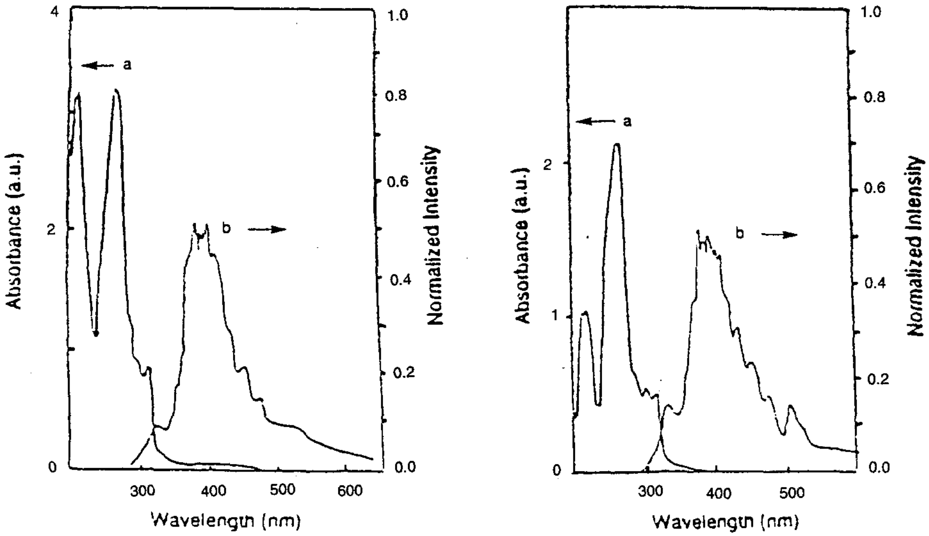


Figure 1. (a) Absorption and (b) Fluorescence ($\lambda_{excitation}$=260 nm) of Copolymer-III (left) and Copolymer-IV (right)

The copolymers are stable to 250°C. Between 250 and 400°C a loss of about 7% is observed. Above 400°C rapid decomposition of I-III occurs. Copolymer IV is more thermally stable. It does not undergo rapid decomposition until 450°C. By 500°C, about 25% of the initial weight of I-III remains. By 550°C, only 20% of the initial weight of IV remains. Above these temperatures, slow further decomposition of I-IV is observed.

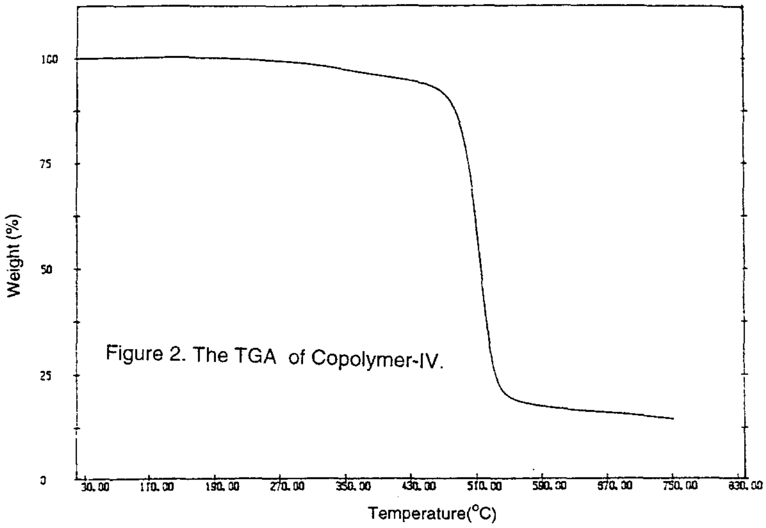


Figure 2. The TGA of Copolymer-IV.

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