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Application of Wittig-Type Reactions of Titanacyclobutane End Groups for the Formation of Block and Graft Copolymers

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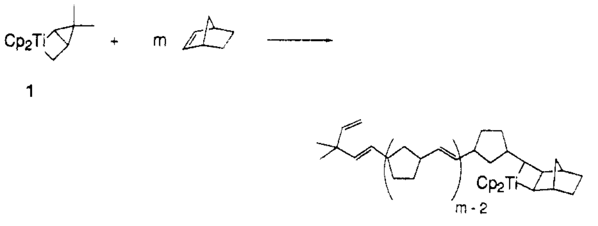
ABSTRACT: Polynorbornene and poly(*exo*-dicyclopentadiene) with one titanacyclobutane end group were linked in a Wittig-type reaction with polymeric ketone groups. The reaction of these living polymers with α,ω-bis(4-benzoylphenyl)poly(oxy-2,6-dimethyl-1,4-phenylene) gave ABA triblock copolymers polynorbornene-*block*-poly(oxy-2,6-dimethyl-1,4-phenylene)-*block*-polynorbornene and poly(*exo*-dicyclopentadiene)-*block*-poly(oxy-2,6-dimethyl-1,4-phenylene)-*block*-poly(*exo*-dicyclopentadiene). Graft copolymers containing polynorbornene side chains were obtained from a reaction with a poly(ether–ketone).

Introduction

Titanium,[1] tungsten,[2] molybdenum,[3] and tantalum[4] complexes have been applied for the living ring-opening olefin metathesis polymerization (ROMP)[5] of norbornene. Bis(η^5-cyclopentadienyl)titanacyclobutane compounds derived from 3,3-dimethylcyclopropene, norbornene, and isobutylene are used as titanium-based initiators[1,6] (eq 1). These initiators produce polymer chains containing a titanacyclobutane end group that is stable at room temperature but is capable of renewed monomer addition when heated above 65 °C. The subsequent addition of different cyclic olefins, such as dicyclopentadiene, benzonorbornadiene, and 6-methylbenzonorbornadiene, resulted in the formation of low-dipersity block copolymers.[7]



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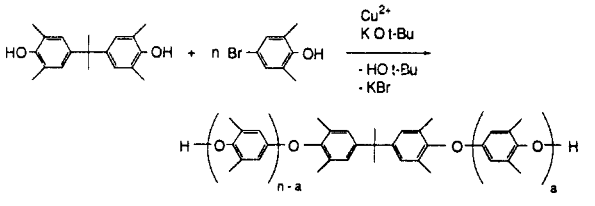
Titanacyclobutanes when heated to the temperature where they cleave to titanium carbene complexes are also known to react with ketones, esters, and amides to form the corresponding olefins, enol ethers, and enamines.[8] Polynorbornene with one diphenylethenyl end group was obtained from the reaction of living polynorbornene with benzophenone.[9]

The present paper describes the application of the Wittig-type reaction for the preparation of block and graft copolymers. Titanacyclobutane structures were used as reactive end groups to link polynorbornene and poly(*exo*-dicyclopentadiene) blocks with polymers containing ketone groups.

Results and Discussion

The hard block poly(oxy-2,6-dimethyl-1,4-phenylene)[10] was selected for the synthesis of ABA triblock copolymers with polynorbornene and poly(*exo*-dicyclopentadiene) segments. The oxidative polymerization of 2,6-dimethylphenol and the dehalogenation polymerization of 4-halo-2,6-dimethylphenol give poly(phenylene ethers) with phenolic hydroxyl end groups.[11] In the past, these aromatic end groups have been utilized for the preparation of block copolymers with polyesters,[12] polycarbonates, and poly(ether–sulfones).[13]

α,ω-Bis(4-benzoylphenyl)poly(phenylene ether) 4 of M_n = 4160 (n = 29) was prepared according to eq 2 and 3. A mixture of 4-bromo-2,6-dimethylphenol and 2,2′,6,6′-tetramethyl-4,4′-isopropylidenediphenol (molar ratio = 25) was polymerized in the presence of catalytic amounts of $CuCl_2$ to give poly(phenylene ether) 3[11b] (eq 2). The experimental value of n is slightly higher than the theoretical value, which corresponds to a monomer ratio of 25. This is probably due to the solubility of the low molecular weight species in methanol, the solvent used for precipitating the polymer. The resulting polymer was reacted with a 50 mol % excess of 4-fluorobenzophenone in a nucleophilic substitution reaction (eq 3). The number of aromatic ketone end groups was determined by ^{1}H NMR spectroscopy. For this purpose, the intensity of the signals at δ 7.75, 7.50, 7.44, and 6.80 (aromatic protons of the end groups) was related to the intensity of the signals at δ 6.42 (aromatic protons of the monomer units) (Figure 1). A value of 1.9 was obtained for the number of ketone end groups for polymer 4.



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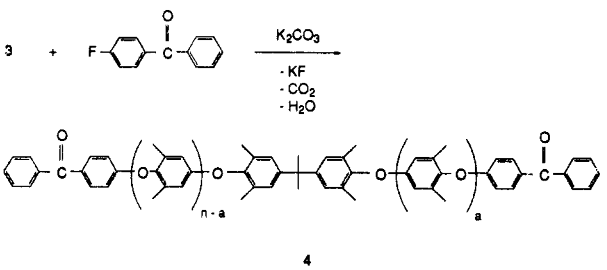

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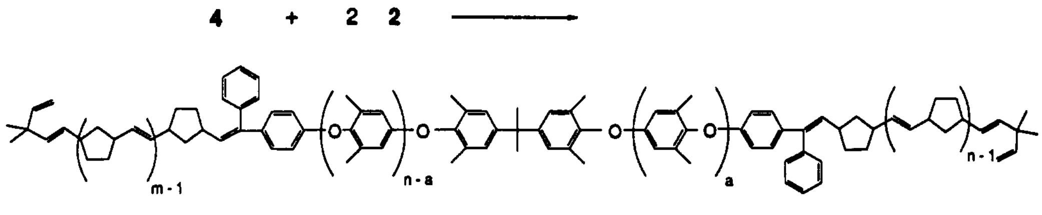

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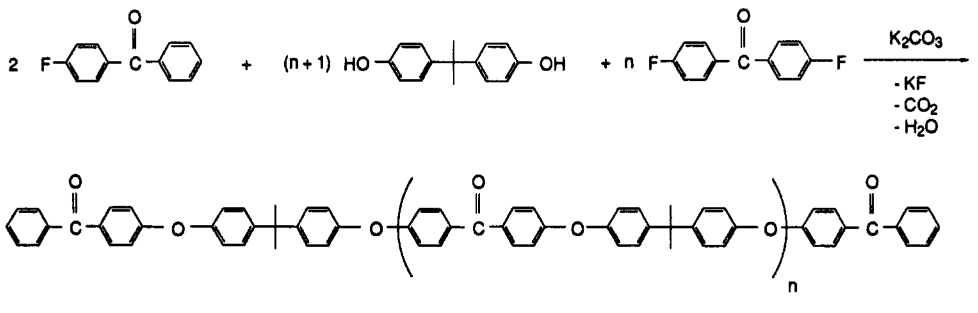

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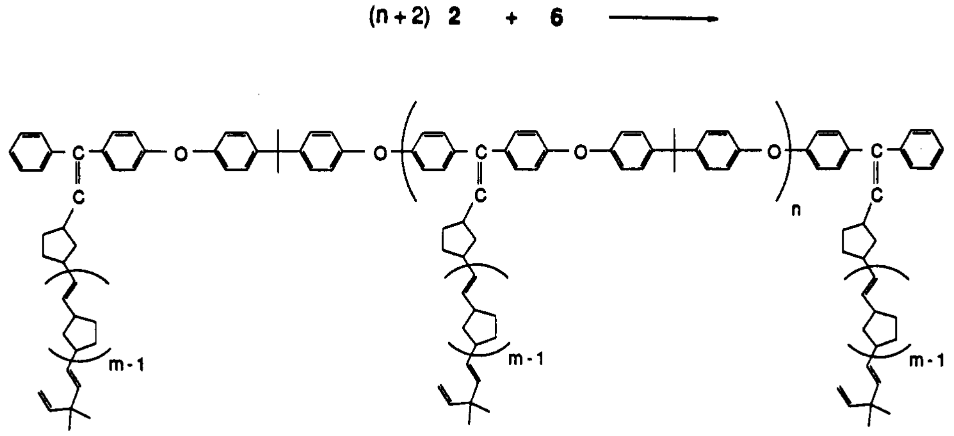

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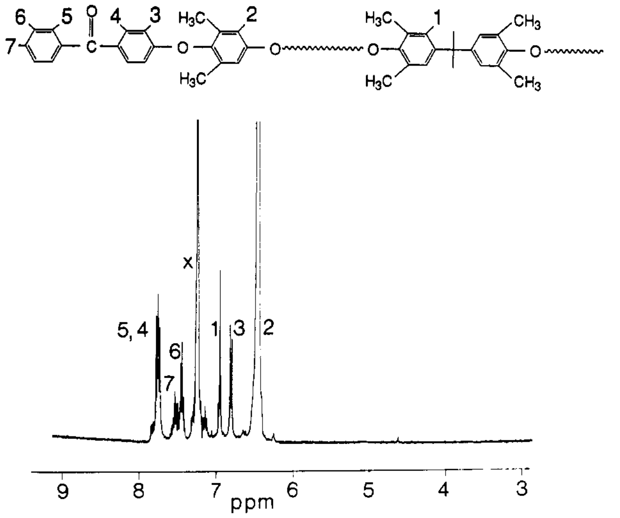

Figure 1. 400-MHz ^{1}H NMR spectrum of the aromatic region of α,ω-bis(4-benzoylphenyl)poly(oxy-2,6-dimethyl-1,4-phenylene) (4) of M_n = 4160 (n = 29) in $CDCl_3$; x = solvent signal.

Norbornene and *exo*-dicyclopentadiene were polymerized with titanacyclobutane 1 to produce polynorbornene (m = 26) and poly(*exo*-dicyclopentadiene) (m = 47) with one titanacyclobutane end group. These blocks were reacted with the α,ω-bis(4-benzoylphenyl)poly(phenylene ether) block at 75 °C. This reaction is shown in eq 4 for polynorbornene.

Triblock copolymers with structures $(NBE)_{26}(DMP)_{29}(NBE)_{26}$, **5**, and $(xDCP)_{47}(DMP)_{29}(xDCP)_{47}$ were obtained (polymers 1 and 2 in Table I; NBE = norbornene, xDCP = *exo*-dicyclopentadiene, DMP = oxy-2,6-dimethyl-1,4-phenylene unit). Table I lists the molecular weights determined for the A blocks produced by olefin metathesis polymerization and the resulting ABA triblock copolymers produced by the Wittig-type reaction. The GPC curves of block copolymer 1 (Table I) and poly(phenylene ether) 4 are compared in Figure 2. The curve of the block copolymer is shifted toward higher molecular weights. A high conversion of the ketone end group was demonstrated for block copolymer 1 of Table I by ^{1}H NMR spectroscopy. The transformation of the aromatic ketone end groups into

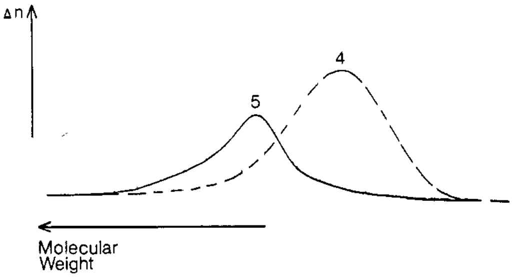

Figure 2. GPC analysis of α,ω-bis(4-benzoylphenyl)poly(oxy-2,6-dimethyl-1,4-phenylene) (4) (broken curve) and polynorbornene-*block*-poly(oxy-2,6-dimethyl-1,4-phenylene)-*block*-polynorbornene (5) (solid curve). The block copolymer was obtained after the Wittig-type reaction of the polymer represented by the broken curve with titanacyclobutane end groups of polynorbornene 2.

Table I
Block and Graft Copolymers Containing Polynorbornene and Poly(*exo*-dicyclopentadiene) Blocks

no.	type[a]	A block[b]	m[c]	M_n(A)[d]	B block[b]	n[c]	M_n(b,g)[d]	PDI[e]	yield, %
1	b	NBE	26	4700	4	29	19100	1.42	87
2	b	*x*DCP	47	12000	4	29	23500	1.50	92
3	g	NBE	46	8350	6	2.7	34800	1.35	92
4	g	NBE	38	6900	6	2.7	28500	1.42	91

[a] ABA triblock copolymer b, graft copolymer g. [b] NBE = norbornene, *x*DCP = *exo*-dicyclopentadiene monomer unit. [c] Number of monomer units m and n present in A block and B block, respectively. [d] M_n(A), M_n(b,g) = number-average molecular weight of A block and the resulting block (b) or graft copolymer (g), respectively, determined by GPC relative to polystyrene; approximate true molecular weights can be obtained by dividing by 1.93.[20] [e] Polydispersity index (M_w/M_n).

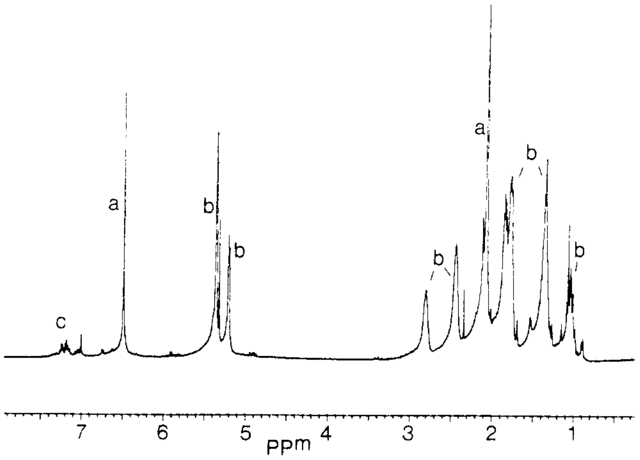

Figure 3. 400-MHz ^{1}H NMR spectrum of polynorbornene-*block*-poly(oxy-2,6-dimethyl-1,4-phenylene)-*block*-polynorbornene (**5**): a = (oxy-2,6-dimethyl-1,4-phenylene) units, b = norbornene units, c = aromatic protons of the linking unit of the polymer blocks.

olefinic groups results in a change of the chemical shifts of the adjacent protons H_3–H_7 from δ 7.75–6.80 (Figure 1) to δ 7.35–7.00 (signals c in Figure 3). Polymer 2 (Table I) showed residual signals (15%) of the 4-benzoylphenyl end group, indicating almost complete reaction.

According to DSC studies, $(NBE)_{26}(DMP)_{29}(NBE)_{26}$ exhibits one glass transition temperature at 70 °C. The miscibility of the two polymer blocks probably results from the low molecular weight of the polynorbornene block. A polymer blend prepared from polynorbornene with M_n = 6300 and poly(oxy-2,6-dimethyl-1,4-phenylene) with M_n = 4200 is phase separated and possesses two glass transitions, T_{g1} = 36 °C (polynorbornene) and T_{g2} = 190 °C (poly(phenylene ether)).

Phase separation was observed for block copolymer 2 of Table I. The glass transition of 113 °C for the *exo*-dicyclopentadiene block of the block copolymer was nearly unchanged from the glass transition of the homopolymer of equal molecular weight (T_g = 108 °C).

Graft copolymers containing polynorbornene blocks were prepared by reacting **2** with the ketone groups of poly(ether–ketone) **6**.[14] Polymer **6** with n = 2.7 (M_n = 1760) was obtained in 42% yield from the nucleophilic substitution reaction of 4-fluorobenzophenone and 4,4′-difluorobenzophenone with 4,4′-isopropylidenediphenol (molar ratio 2:1:2) (eq 5). Fractionation with methanol resulted in a reduced yield and, accordingly, in a higher value for the number of repeat units (n = 2.7 instead of 1). The reaction of polynorbornene **2** (m = 46 and 38) gave graft copolymer **7** (polymers 3 and 4 of Table I) with a poly(aryl ether) backbone (eq 6). Both graft copolymers show an approximately fourfold increase in the molecular weight when compared with the A blocks prepared by olefin metathesis (Table I). Assuming complete conversion of the ketone groups of the poly(ether–ketone) block, graft copolymers 3 and 4 of Table I are expected to possess an average of 4.7 polynorbornene side chains. The high percent of conversion of the ketone groups was determined by ^{1}H NMR spectroscopy in a similar way as for the block copolymers. No aromatic protons ortho to a carbonyl group could be detected. No residual homopolymer of polynorbornene could be detected by GPC analysis of graft copolymer **7**. A small shoulder at M_n = 17000 corresponds to a minor amount (approximately 5 mol %) of polymer with two polynorbornene side arms (n = 0).

DSC studies of **7** exhibited one glass transition temperature,[15] T_g = 40 °C, which is slightly higher than the glass transition of the pure polynorbornene block (T_g = 36 °C).

Conclusion and Outlook

Titanacyclobutane structures were introduced as a new class of reactive end groups for the Wittig-type reaction with polymer-bound ketone groups. ABA triblock copolymers were obtained from the reaction with a polymer containing two ketone end groups. Polymers containing ketone groups within the polymer chain resulted in graft copolymers.

Future applications of this reaction for linking polymer blocks can result in the synthesis of new block copolymer structures, including thermoplastic elastomers, when hard blocks A are combined with soft segments B to form ABA- or $(AB)_n$-type block copolymers.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed by using standard high-vacuum, Schlenk, or drybox (Vacuum Atmospheres) techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. ^{1}H NMR spectra were recorded on a JEOL GX-400 (399.65 MHz) spectrometer. Gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use (column: 0.25 mm × 50 m DBI, SE 30) and equipped with a Hewlett-Packard Model 339A integrator. Flash chromatography was performed by the procedure of Still et al.[16] using silica gel 60 (230–400-mesh ATM, EM Reagents). Gel permeation chromatographic (GPC) analyses utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on 0.5% (w/v) solutions of polymer in dichloromethane. An injection volume of 0.1 mL and a flow rate of 1.5 mL/min were used. Calibration was based on narrrow dispersity polystyrene standards (Polysciences) ranging from M_n = 3500 to 600000. The molecular weight averages and distributions were calculated by standard procedures[17] from the refractive index and were not corrected for peak broadening.

Vapor-phase osmometry (VPO) was performed on polymer solutions in benzene (concentration range: 10^{-3}–10^{-2} mol/L) at 47 °C using a Wescan Molecular Weight Apparatus Model 233. Transition temperatures were determined under a nitrogen atmosphere on a Perkin-Elmer Delta Series DSC 7 at a heating rate of 20 °C/min. Oil bath temperatures for all polymerizations were maintained at a constant value (±0.2 °C) by use of a I^2R Therm-O-Watch.

Materials. Metallacycle **1** was prepared from Tebbe reagent and 3,3-dimethylcyclopropene as previously described.[6] 3,3-Dimethylcyclopropene was kindly provided by S. C. Virgil. Norbornene (Aldrich) was refluxed over sodium and distilled prior to use. *exo*-Dicyclopentadiene (Wiley Organics, 95% exo, 5% endo) was stirred over sodium for 12 h and then vacuum-distilled. These olefins were deoxygenated by three freeze–pump–thaw-degassing cycles and stored in the drybox. 4-Bromo-2,6-dimethylphenol was prepared as previously described.[18] 4,4′-Isopropylidenediphenol (Aldrich) was recrystallized from toluene. 2,2′,6,6′-Tetramethyl-4,4′-isopropylidenediphenol was kindly provided by Bayer AG. 4-Fluorobenzophenone (Aldrich) was recrystallized from *n*-heptane/ethanol (2/1 volume ratio). Methanol for the precipitation of polymers and anhydrous potassium carbonate was reagent grade and used without further purification. Toluene and toluene-d_8 were vacuum transferred from sodium benzophenone ketyl. Toluene for olefin metathesis polymerization was further purified by vacuum transferring from "titanocene".[19] DMSO (Aldrich, Gold label grade) was used as obtained from the manufacturer. α,ω-Dihydroxypoly(oxy-2,6-dimethyl-1,4-phenylene), **3**, was prepared from 4-bromo-2,6-dimethylphenol and 2,2′,6,6′-tetramethyl-4,4′-isopropylidenediphenol (molar ratio 25:1) as previously described.[11b]

Preparation of α,ω-Bis(4-benzoylphenyl)poly(oxy-2,6-dimethyl-1,4-phenylene) (4). A 100-mL Schlenk flask, equipped with a magnetic bar, a distillation head, and a receiving flask, was charged with 1 g (0.27 mmol) of poly(phenylene ether) **3**, 300 mg (2.18 mmol) of anhydrous potassium carbonate, 162 mg (0.81 mmol) of 4-fluorobenzophenone, 10 mL of toluene, and 15 mL of DMSO. The mixture was stirred under argon for 1 h in an oil bath at 160 °C. The reaction mixture turned green. First a toluene/water mixture, and then pure toluene, distilled off. After cooling, the heterogeneous mixture was poured into 70 mL of methanol of precipitate crude polymer **4**. The product was redissoved in 10 mL of chloroform, and the unreacted potassium carbonate was removed by filtration. Polymer **4** was isolated by reprecipitation with methanol and dried under vacuum (10^{-3} Torr) for 48 h: yield 1.01 g (92%), $M_n = 4160$ (vapor-phase osmometry); ^1H NMR ($CDCl_3$) δ 7.75 (m, 1.9[21] × 4 H); 7.50 (m, 1.9 × 1 H), 7.44 (m, 1.9 × 2 H), 6.96 (s, 4 H), 6.80 (d, $J = 9$ Hz, 1.9 × 2 H), 6.42 (s, 29[22] × 2 H), 2.07 (s, 31 × 6 H), 1.68 (s, 6 H).

Preparation of Triblock Copolymer 5 ($(NBE)_{26}(DMP)_{29}(NBE)_{26}$). A heavy-walled flask with a Teflon valve closure was charged with 52 mg (0.2 mmol) of titanacyclobutane **1** and 1.5 mL of a solution of 567 mg (6.03 mmol) of norbornene in toluene. Toluene was added to give a total volume of 4 mL. By syringe, 1 mL of the solution was transferred into a second identical flask. Both flasks were heated in an oil bath at 75 °C. The polymerization was followed by capillary VPC. After 87% conversion, the polymerization was stopped by cooling. Poly(phenylene ether) **4** (312 mg, 0.075 mmol) was added to the reaction mixture prepared from 3 mL of the initial solution and heated for 30 min at 75 °C. The color of the solution turned from deep red to bright orange. The second polymerization sample was end-capped by adding 58 mg of acetone and heating at 75 °C for 30 min. After cooling, both solutions were flash chromatographed (toluene) and the polymers isolated by precipitation with methanol. The polymers were dried under vacuum (10^{-3} Torr) for 24 h. The yield was 593 mg (87%) of block copolymer (polymer 1 of Table I) and 89 mg (63%) of acetone-capped polynorbornene (reference sample). Block copolymer 2 of Table I was prepared by using the same procedure.

Preparation of Poly(ether–ketone) 6. A mixture of 1.37 g (6 mmol) of 4,4′-isopropylidenediphenol, 645 mg (3 mmol) of 4,4′-difluorobenzophenone, 1.2 g (6 mmol) of 4-fluorobenzophenone, 1.66 g (12 mmol) of anhydrous potassium carbonate, 30 mL of DMSO and 20 mL of toluene was heated to 170 °C. The water formed was removed as an azeotrope with toluene by using a Dean Stark trap. After 1 h, pure toluene distilled off. Stirring at 170 °C was continued for 1 h. The mixture was cooled and the polymer precipitated with 150 mL of methanol. Unreacted potassium carbonate was removed in the same way as in the preparation of **4**: yield 1.25 g (42%); $M_n = 1760$ (vapor-phase osmometry); ^1H NMR ($CDCl_3$) δ 7.78 (m, 4.7[23] × 4 H (includes end groups)), 7.55 (m, 2 × 1 H (end groups)), 7.48 (m, 2 × 2 H (end groups)), 7.28 (m, 3.7 × 4 H), 7.00 (m, 7.4 × 4 H), 1.71 (s, 3.7 × 6 H).

Preparation of Graft Copolymer 7. Two samples (a main sample and a reference sample) were polymerized in parallel reactions at 75 °C in the same manner as for the preparation of **5**. The initial main sample (1.5 mL of overall volume) contained 181 mg (1.92 mmol) of norbornene and 8.6 mg (0.033 mmol) of titanacycle **1** in toluene (the reference sample (0.5 mL of volume) contained (0.48 mmol) of norbornene and 2.1 mg (8.1 μmol) of **1** in toluene). After 79% conversion, 12.4 mg of poly(ether–ketone) **6** was added to the main sample. The mixture was heated for 30 min at 75 °C and the polymer isolated as described for the synthesis of **5**. The reference sample was end-capped with 20 mg of acetone. The yield was 142 mg (92%) of graft copolymer and 29 mg (82%) of acetone-capped polynorbornene. The same procedure was applied for the synthesis of graft copolymer 4 of Table I: ^1H NMR (CD_2Cl_2) δ 7.35–7.10 (m), 6.93 (bs), 6.88 (bs) (poly(aryl ether)) backbone; 5.37 (bs), 5.21 (d, $J = 6$ Hz), 2.81 (bs), 2.45 (bs), 1.82 (bm), 1.36 (bm), 1.04 (bm) (polynorbornene side chain).

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Registry No. **4**, 123027-86-1; **5** (block copolymer), 123027-84-9; **6**, 123027-87-2; (DMP)(DCP) (block copolymer), 123027-85-0; (4,4′-difluorobenzophenone)(4,4′-isopropylenediphenol) (graft copolymer), 121065-81-4.

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(21) Average number of end groups = 1.9 (±10%).
(22) 29 monomer units of oxy-2,6-dimethyl-1,4-phenylene.
(23) *n* repeat units (2.7) + 2.

Heat-Resistant Polymers Prepared from [(4′-(2-Vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene

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ABSTRACT: The radical-initiated copolymerization of [(4′-(2-vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (**2**) with styrene or methyl methacrylate in 1,2-dichloroethane and the thermal behavior of their copolymers were investigated. The copolymers, poly(**2**-*co*-St) and poly(**2**-*co*-MMA), were found to be enriched in **2** with respect to the monomer feed. The comparison of Alfrey–Price parameters of **2** with those of 4-hydroxy-4′-vinylbiphenyl (**1**) suggests that the phosphazene ring in **2** acts only as an electron-withdrawing group. The thermogravimetric analysis indicates that incorporation of **2** in the copolymers leads to increased thermal stability. The copolymers containing more than 50 mol % of **2** afford 56–65% char yields at 800 °C in air or nitrogen atmosphere.

Introduction

There has been considerable interest in poly(organophosphazenes).[1-7] These polymers often exhibit useful, interesting properties, such as flame retardency, high thermal stability, and resistance to chemicals. Attempts to improve the thermal stability and flame retardency of polymers by incorporation of a cyclotriphosphazene moiety have been demonstrated.[8-13] For example, the polymer obtained from maleimide-substituted aromatic cyclotriphosphazene has good thermal stability and affords a residue with high yield at 800 °C.[8,9] Furthermore, Allen et al.[10-13] have examined the thermal behavior of the copolymers with the pendant pentafluorocyclotriphosphazene unit, which were prepared by a conventional radical copolymerization. Although the incorporation of the phosphazene moiety imparts flame-retardant properties to the copolymers, significant improvement in the thermal stability of these copolymers over that of the organic homopolymer was not observed.

In the previous papers,[14,15] we reported that the radical polymerization of [(4′-(2-vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (**2**; Scheme I) and the thermal behavior of its polymer showed that **2** has a high-radical polymerizability and that poly(**2**) is thermally stable up to 300–400 °C, depending on the molecular weight. Of particular interest is the fact that the polymer gives a residue with high yield (60%) at 800 °C in both air and nitrogen atmospheres. From these results one would expect that the copolymers containing the desired content of **2** could be prepared and show improved thermal stability relative to the organic homopolymer.

In this paper, we describe the copolymerization of **2** with styrene or methyl methacrylate with AIBN initiation and the thermal behavior of their copolymers. Furthermore, the thermal stability of blend polymer of poly(**2**) and polystyrene is also described.

Table I
Conditions and Results of Copolymerization of 2 with Styrene in 1,2-Dichloroethane at 70 °C[a]

mol % of 2 in monomer feed	mol % of 2 in copolymer	conversion for 6 h, %	$10^{-4}\bar{M}_n$ [b]	$10^{-4}\bar{M}_w$ [b]	$\bar{M}_w/\bar{M}_n$
5	11.5	12.2	1.0	1.4	1.4
10	20.7	12.0	1.1	1.6	1.4
15	29.6	14.0	1.3	1.9	1.5
20	37.2	14.6	1.5	2.2	1.5
30	49.8	16.2	1.9	5.5	2.9
40	59.9	20.6	2.5	4.3	1.7
50	68.8	23.5	2.8	5.8	2.1
60	76.4	28.8	3.6	8.0	2.2
70	82.9	36.1	4.4	9.4	2.1
90	94.6	50.7	6.5	16.7	2.6

[a] [**2**] + [St] = 0.4 M, [AIBN] = 2 mM. [b] Determined by GPC.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was kindly provided by Nippon Soda Co. and used without further purification. [(4′-(2-Vinyl)-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (**2**) was prepared from 4-hydroxy-4′-vinylbiphenyl (**1**)[16] and hexachlorocyclotriphosphazene. Details of preparation and characterization of **2** were described in the previous paper.[14] AIBN was recrystallized from methanol. Styrene and methyl methacrylate were distilled before use. Other chemicals were purified by known procedures.

Copolymerization. Copolymerization of **2** with St or MMA in 1,2-dichloroethane was run at 70 °C in tubes sealed under vacuum, with AIBN as initiator (Tables I and II). The copolymer was obtained by precipitation from hexane.

Measurements. Infrared spectra were recorded on a Shimadzu IR-420 spectrophotometer. UV spectra were obtained on a Shimadzu UV-260 spectrophotometer. Gel permeation chromatography was performed on a Shimadzu LC-3A instrument equipped with UV and RI detectors, using THF as eluent. The columns consisted of Shimadzu HSG 60 and 30 (MW range, 1×10^3–1×10^6). The columns were calibrated with polystyrene

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