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Novel Poly(*p*-xylylenes): Thin Films with Tailored Chemical and Optical Properties

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ABSTRACT: Chemical vapor deposition polymerization is used to prepare submicron thin films of poly(*p*-xylylenes) with distinct chemical and optical properties. The polymers are prepared from 13 different [2.2]paracyclophanes with variable degrees of substitution and functionalities including hydroxy, methoxy, amino, triflate, or trifluoroacetyl groups. The chemical composition of the poly(*p*-xylylenes) is in good accordance with expected chemical structures as confirmed by X-ray photoelectron spectroscopy, microanalysis, and reflection−absorption infrared spectroscopy. For all polymers, basic optical properties, such as extraordinary and ordinary indices of refraction, are reported and reveal optical anisotropy of the coatings. Experimental data correlate well with data generated by a uniaxial Cauchy dispersion model. Furthermore, a distinct correlation between refractive indices and the electronic properties of the functional groups is observed. Similarly, optical birefringence depends on the nature of the functional group as significant variation in optical birefringence was found among the reported poly(*p*-xylylenes).

Introduction

Thin-film polymer coatings are currently studied as templates for several high-tech applications including biomaterials,[1] insulating layers in integrated circuits[2] and thin-film transistors,[3] light-emitting diodes,[4,5] optical or microelectrical−mechanical systems (MEMS),[6] lasers,[7,8] waveguides,[9] and photodiodes.[10] Poly(*p*-xylylenes) belong to a group of special polymers that are under investigation for thin-film applications. Some members of this polymer family have gained commercial acceptance due to their high solvent resistance, low dielectrical constants, and good barrier properties.[11] Although poly(*p*-xylylenes) can be prepared in solution, e.g., electrochemically,[12] chemical vapor deposition (CVD) polymerization is the preferred preparation method for thin-film applications.[13] CVD polymerization is a room temperature process that requires no catalyst, solvent, or initiator and can generally be carried out without production of byproducts. Well-defined and chemically robust polymer films can be deposited by this method; suitable monomers include α,α′-dihydroxy-*p*-xylylenes,[14] α,α′-dibromo-*p*-xylylenes,[15] α,α′-diacetoxy-*p*-xylylenes,[16] and [2.2]paracyclophanes.[17]

Thin-film coatings that provide free functional groups for surface modification may represent attractive templates for surface engineering. In an attempt to prepare functionalized coatings, CVD polymerization was used to prepare alkylated and acetylated poly(*p*-xylylenes)[17] as well as germanium- and silicon-substituted polymers.[18,19] We synthesized amino- and hydroxy-substituted poly(*p*-xylylenes)[20,21] and used these polymer films as interfaces for protein attachment[22] or for patterning of polymer brushes onto a CVD-coated substrate.[23] Recently, this technological platform was extended further when *reactive coatings* (i.e., poly(*p*-xylylenecarboxylic acid pentafluorophenol ester-*co*-*p*-xylylene)[24] and poly(*p*-xylylene-2,3-dicarboxylic acid anhydride)[25]) were prepared. Their intrinsic chemical reactivity supports rapid reaction with biological ligands or proteins and was used for surface modification using microcontact printing.[26] However, the overall impact of this technology in surface engineering may depend on how variable poly(*p*-xylylenes) with different functional groups can be prepared, enabling different binding modes for attachment of biomolecules. The motivation of this paper is to examine and broaden the variety of polymer films prepared by CVD polymerization and to study their basic optical properties.

Materials and Methods

Materials. If not indicated differently, chemicals were purchased from Aldrich, Milwaukee, WI, and were used without further purification. Gold substrates were prepared from silicon wafers (Silicon Quest Int., Santa Clara, CA) by deposition of a sequence of silicon nitride (200 nm), titanium (10 nm), and gold (100 nm).

[2.2]Paracyclophane-4-carboxylic Acid Methyl Ester (1d): 950 mg of **1c** was dissolved in 20 mL of methanol, and 2 mL of a solution of hydrogen chloride in ether (2 M) was added. The solution was stirred for 12 h under reflux, and the crude product was isolated by filtration. Drying under vacuum at 50 °C and subsequent column chromatography (silica gel, chloroform/hexane, 1:1 (v:v)) delivered 608 mg of product **1d**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.85-2.95$ (m, 1H, CH_2), 3.00−3.23 (m, 7H, CH_2), 3.93 (s, 3H, CH_3), 4.13 (t, 2H, CH_2O), 6.55 (m, 4H, CH), 6.68 (d/d, 2H, CH), 7.28 (s, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 35.37$, 35.51, 36.67, 36.54, 52.19, 129.21, 131.96, 132.68, 133.13, 133.51, 135.71, 136.54, 136.84, 139.78, 140.69, 142.50, 168. IR (KBr): $\nu = 508$, 723, 871, 1004, 1112, 1127, 1199, 1271, 1327, 1440, 1721, 2955, 2996 cm^{-1}. MS (70 eV): $m/z = 266$ (M^+), 251 (M^+-CH_3), 235 ($C_{16}H_{15}CO^+$), 162 ($C_8H_7COOCH_3{}^+$), 147 (162−CH_3), 119 (C_8H_8-$CH_3{}^+$), 104 (main, $C_8H_8{}^+$), 103 ($C_8H_7{}^+$), 78 ($C_6H_6{}^+$), 77 ($C_6H_6{}^+$).

(Methylcarbonyloxy)[2.2]paracyclophane (1g): 500 mg of **1f** was added to a solution of 30 mL of anhydrous acetic acid anhydride and 3 mL of anhydrous pyridine. The solution was stirred at 130 °C for 12 h. The reaction mixture was quenched with aqueous sodium bicarbonate solution (1 N). Extraction with ethyl acetate and subsequent chromatographic purification (silica gel, chloroform/hexane, 4:1 (v:v)) delivered 555 mg of **1g**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.13$ (s, 3H, CH_3), 2.96−3.21 (m, 7H, CH_2), 3.22−3.36 (m, 1H, CH_2),

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Table 1. Representative Parameters Used for CVD Polymerization of [2.2]Paracyclophanes

functionality	polymer	precursor	purity of precursor (%)	amount of precursor (mg)	sublimation temp (°C)	pyrolysis temp (°C)	substrate temp (°C)	system pressure (mbar)	argon mass flow (sccm)[a]
alcohol	**2a**	**1f**	100	56	220	750	20	0.08	10.0
methyl ether	**2b**	**1j**	99	30	240	720	20	0.1	0.5
acetate	**2c**	**1g**	100	55	260	610	15	0.2	1.2
methyl ester	**2d**	**1d**	100	50	275	670	15	0.11	2.0
tetramethyl ester	**2e**	**1o**	100	50	325	670	15	0.12	2.0
anhydride	**2f**	**1p**	95	36	340	620	12	0.2	4.5
lactone	**2g**	**1q**	98	30	355	750	12	0.05	5.0
amine	**2h**	**1m**	100	59	270	700	20	0.2	15.0
diamine	**2i**	**1n**	95	39	280	620	15	0.12	2.0
pentafluorophenol ester	**2j**	**1e**	99	50	230	600	12	0.12	2.0
trifluoroacetate	**2k**	**1h**	95	70	248	720	15	0.10	8.0
triflluoromethyl ketone	**2l**	**1b**	99	60	240	650	20	0.12	2.0
triflate	**2m**	**1i**	100	60	340	650	12	0.07	0.9
unsubstituted	**2n**	**1a**	100	20	270	750	20	0.07	7.0

[a] sccm = standard cubic centimeter.[20]

5.13 (d, 1H, CH_2O), 5.30 (d, 1H, CH_2O), 6.42 (2, 2H, CH), 6.55 (m, 5H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 33.35$, 34.89, 35.39, 35.69, 65.94, 130.74, 132.65, 133.32, 133.59, 133.78, 134.30, 134.74, 135.46, 137.43, 139.62, 139.95, 140.59, 171.49. IR (KBr): $\nu = 608$, 615, 718, 871, 1025, 1235, 1250, 1368, 1414, 1634, 1731, 1900, 2858, 2940, 3007 cm^{-1}. MS (70 eV): $m/z = 280$ (M^+), 220 ($C_{17}H_{17}^+$), 176 ($C_8H_7CH_2OCOCH_3^+$), 148 ($C_8H_7CH_2CH_2OH$), 115 ($C_9H_7^+$), 104 (main, $C_8H_8^+$), 103 ($C_8H_7^+$), 78 ($C_6H_6^+$), 77 ($C_6H_6^+$).

(Trifluoromethylcarbonyloxy)[2.2]paracyclophane (1h): 500 mg of **1f** was dissolved in 30 mL of tetrahydrofuran, and 5 mL of trifluoroacetic anhydride was added at 0 °C. After 10 min, the solvent was removed in a vacuum, and the residue was dissolved in diethyl ether. The solution was extracted with aqueous sodium bicarbonate (1 M) and sodium chloride (1 M) solutions. Column chromatography (silica gel, chloroform/hexane, 1:1 (v:v)) delivered 683 mg of the pure product **1h**. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.97-3.16$ (m, 7H, CH_2), 3.20−3.36 (m, 1H, CH_2), 5.13 (d, 1H, CH_2O), 5.32 (d, 1H, CH_2O), 6.41 (s, 2H, CH), 6.55 (t, 3H, CH), 6.58 (d, 1H, CH), 6.63 (d, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 33.20$, 34.90, 35.76, 35.59, 69.07, 129.95, 131.96, 132.42, 133.42, 133.63, 134.14, 134.33, 135.57, 138.87, 139.23, 139.85, 140.68, 160. IR (KBr): $\nu = 646$, 733, 774, 907, 1163, 1214 1342, 1399, 1496, 1593, 1778, 1911, 2858, 2925, 2955 cm^{-1}. MS (70 eV): $m/z = 334$ (M^+), 230 ($C_8H_7CH_2OCOCF_3^+$), 133 ($C_9H_8OH^+$), 115 (133-H_2O), 104 (main, $C_8H_8^+$), 78 ($C_6H_6^+$).

(Trifluoromethylsulfoxyloxy)[2.2]paracyclophane (1i): 500 mg of **1f** was dissolved in 30 mL of methylene chloride, and 5 mL of triflic anhydride was added at 0 °C. After 10 min, solvent was removed in a vacuum, and the residue was dissolved in diethyl ether and extracted with aqueous sodium bicarbonate (1 M) and sodium chloride (1 M) solutions. Column chromatography (silica gel, chloroform/hexane, 1:1 (v:v)) delivered 710 mg of the pure product **1i**. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.80-3.20$ (m, 7H, CH_2), 3.25−3.40 (m, 1H, CH_2), 5.60 (d, 1H, CH_2O), 5.90 (d, 1H, CH_2O), 6.40 (s, 1H, CH), 6.45−6.63 (m, 2H, CH), 6.75 (d, 1H, CH), 8.10 (t, 1H, CH), 8.57 (t, 1H, CH), 9.00 (d, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 31.53$, 32.81, 33.20, 33.57, 61.17, 127.50, 128.63, 131.18, 131.84, 132.03, 132.74, 133.99, 134.49, 137.58, 138.01, 139.83, 143.80, 144.58, 149.99. IR (KBr): $\nu = 518$, 636, 687, 753, 1030, 1143, 1230, 1265, 1496, 1639, 2858, 2925, 3068 cm^{-1}.

4-Methoxymethyl[2.2]paracyclophane (1j): 478 mg of **1f** was dissolved in 100 mL of methylene chloride, and 2.143 g of bis(dimethylamino)naphthalene and 1.479 g of trimethyloxonium tetrafluoroborate were added. The solution was stirred for 3 h at room temperature and subsequently quenched by adding 20 mL of aqueous sodium carbonate (1 M). Extraction with methylene chloride, drying over sodium sulfate, and column chromatography (silica gel, chloroform/hexane, 3:1 (v:v)) delivered 350 mg of **1j**. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.80-2.94$ (m, 1H, CH_2), 2.97−3.21 (m, 7H, CH_2), 3.38 (s, 3H, CH_3), 4.18 (d, 1H, CH_2O), 4.53 (d, 1H, CH2O), 6.43 (m, 2H, CH), 6,50 (s, 1H, CH), 6.53 (d/d, 2H, CH), 6.58 (d/d, 1H, CH), 6.68 (d/d, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 33.29$, 34.83, 35.46, 35.73, 58.77, 74.49, 129.50, 132.54, 132.66, 133.58, 133.62, 133.68, 135.27, 137.34, 138.36, 139.72, 139.97, 140.26. IR (KBr): $\nu = 513$, 651, 723, 902, 758, 799, 876, 1120, 1097, 1189, 1260, 1352, 1409, 1496, 1593, 1731, 1890, 2735, 2849, 2918 cm^{-1}; MS (70 eV): $m/z = 252$ (M^+), 237 (M^+-CH_3), 222 (M^+-CH_2O), 207 ($C_{16}H_{15}^+$), 165 (C_8H_7-$COOCH_3^+$), 147 ($C_9H_8OCH_3^+$), 134 ($C_8H_7CH_2OH^+$), 133 (C_9H_8-OH^+), 118 (main, $C_8H_7CH_3^+$), 104 ($C_8H_8^+$), 78 ($C_6H_6^+$), 77 ($C_6H_6^+$), 51.

[2.2]Paracyclophane-4,5,12,13-tetracarboxylic γ-Butyryl Lactone (1q): 500 mg of **1p** was suspended in 45 mL of tetrahydrofuran. 65 mg of sodium borohydride dissolved in 10 mL of tetrahydrofuran was added, and the reaction mixture was stirred for 19 h at room temperature. The reaction mixture was quenched with aqueous hydrogen chloride (6 N). Extraction with ethyl acetate and subsequent chromatographic purification (silica gel, methyl sulfoxide/methylene chloride, 2:1 (v:v)) yielded 72% of **1q**. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.83-3.18$ (m, 6H, CH_2), 3.74 (m, 2H, CH_2), 5.13 (m, 4H, CH_2O), 6.44 (m, 2H, CH), 7.10 (m, 2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 29.05$, 30.30, 69.91, 131.68, 133.39, 134.45, 135.17, 135.98, 139.97, 167.82. IR (KBr): $\nu = 687$, 794, 979, 1025, 1066, 1143, 1240, 1363, 1450, 1491, 1578, 1747, 2858, 2930 cm^{-1}. MS (70 eV): $m/z = 320$ (M^+), 302 (M^+-H_2O), 160 ($^1/_2$ M^+), 131, 115 ($C_9H_7^+$), 104 ($C_8H_8^+$), 103 ($C_8H_7^+$), 78 ($C_6H_6^+$), 77 ($C_6H_6^+$).

Synthesis of [2.2]paracyclophanes **1b**, **1c**, **1e**, **1f**, and **1k**−**1p** is described in detail elsewhere.[20,24,25,27] All products were characterized by infrared, nuclear magnetic resonance spectroscopy (^1H and ^{13}C), and mass spectrometry. The spectroscopic data were in accordance with literature data.[20,24,25,27] The purity of [2.2]paracyclophanes used for CVD polymerization was above 95% as determined by gas chromatography.

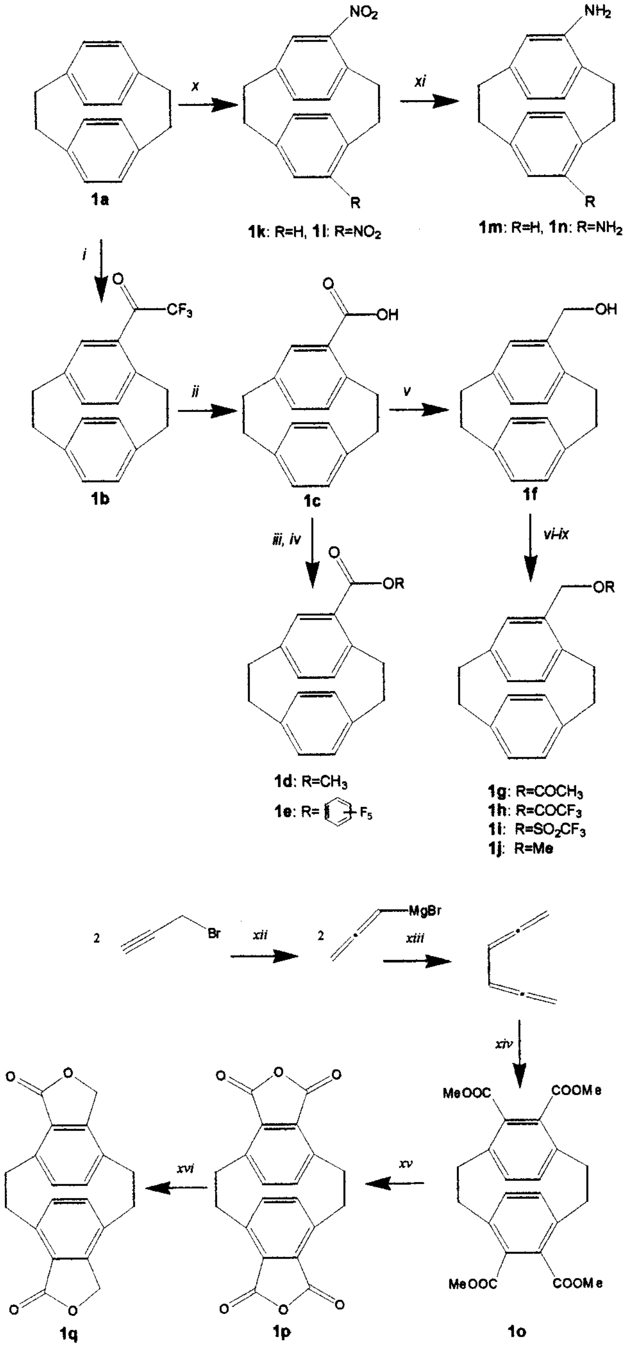
CVD Polymerization. Polymers were obtained from the corresponding [2.2]paracyclophanes by CVD polymerization using an installation consisting of a sublimation zone, a pyrolysis zone, and a deposition chamber.[22] Polymerization parameters are summarized in Table 1. The pyrolysis of the [2.2]paracyclophanes was carried out in a furnace with three independently regulated heating zones to ensure a nearly constant temperature profile. The polymerization chamber is equipped with a rotating, cooled sample holder, an on-line thickness monitor (Sycon Instruments, New York), and a temperature and vacuum gauge. Its walls were kept above 110 °C to avoid undirected deposition. For polymerization, a defined amount of starting material was placed in the sublimation zone, and a substrate was fixed on the sample holder at a particular temperature. A defined argon flow was used as carrier gas, the pressure was adjusted, and the pyrolysis zone was heated. Subsequently, starting material was slowly sublimed by increasing the temperature of the sublimation zone. Polymerization resulted in transparent polymer films on the substrate.

Surface Characterization. X-ray photoelectron spectroscopy (XPS) data were recorded on an Axis Ultra X-ray photoelectron spectrometer (Kratos Analyticals) equipped with an Al Kα X-ray source. The pass energy was 160 eV for survey spectra and 10 eV for high-resolution spectra. All spectra were calibrated in reference to the unfunctionalized aliphatic carbon at a binding energy of 285.0 eV. The emission angle of electrons was set at 55°, which results in an information depth of about 6 nm. Reflection−absorption infrared spectroscopy (RAIRS) was done on a Magna 550 spectrometer (Nicolet) equipped with a grazing angle accessory (Spectra-Tech) under a grazing angle of 85°. Microanalysis was conducted on polymers deposited as thick films (thickness > 1 μm) on glass slides. The polymers were carefully separated from the substrate using a razor plate. Spectroscopic ellipsometry was carried out on a variable angle spectroscopic ellipsometer (J.A. Woollam Inc.) using a uniaxial Cauchy model for curve fitting. Wavelengths between 350 and 800 nm and three angles (65°, 70°, and 75° with respect to sample normal) were examined. Polymer films were deposited on silicon wafers for examination. The silicon model was modeled by assuming a 1 mm silicon bulk with a thin native oxide layer (17 nm).[28] Root-mean-square errors (RSE) were below 20 for all samples included in this study.

Results and Discussion

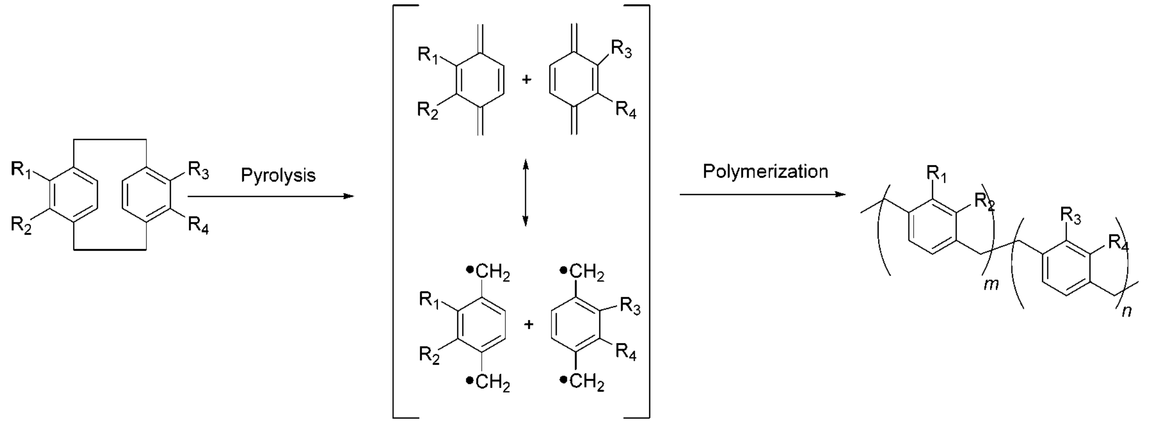
Synthesis of Functionalized [2.2]Paracyclophanes. Friedel−Crafts acylization of [2.2]paracyclophane (**1a**) with trifluoroacetic acid anhydride using an excess of $AlCl_3$ resulted in 4-trifluoroacetyl[2.2]paracyclophane (**1b**) in 92% yields (Scheme 1). Subsequent hydrolysis of **1b** under basic aqueous conditions led to 4-carboxy[2.2]paracyclophane (**1c**) (93% yields). Acid-catalyzed esterification with methanol resulted in [2.2]paracyclophane-4-carboxylic acid methyl ester (**1d**) in yields of 60%. [2.2]Paracyclophane-4-carboxylic acid pentafluorophenolester (**1e**) was then synthesized by conversion of compound **1c** with pentafluorophenol trifluoroacetate.[24] As shown in Scheme 1, compound **1c** served as starting material in the synthesis of 4-hydroxymethyl[2.2]paracyclophane (**1f**) and its derivatives. Reduction of **1c** with lithium aluminum hydride in tetrahydrofuran yielded compound **1f** in 95%. Esterification of compound **1f** under mild conditions with either acetic acid anhydride, trifluoroacetic acid anhydride (0 °C), or triflic acid anhydride (0 °C) resulted in (methylcarbonyloxy)[2.2]paracyclophane (**1g**), (trifluoromethylcarbonyloxy)[2.2]paracyclophane (**1h**), and (trifluoromethylsulfoxyloxy)[2.2]paracyclophane (**1i**), respectively. The yields of these reactions were between 94 and 97%. 4-Methoxymethyl[2.2]paracyclophane (**1j**) was synthesized from **1f** by etherification. Trimethyloxonium tetrafluoroborate in combination with the bulky tertiary base bis(dimethylamino)naphthalene as catalyst proved to be an efficient etherification agent under gentle reaction conditions (yield: 69%). Mono- or dinitro[2.2]paracyclophane (**1k**−**l**) was synthesized at low temperatures by nitration of **1a** under superacidic conditions.[27] Using the superacidic ion-exchange resin Nafion/nitric acid, compound **1k** is obtained in 95% yield. Synthesis of compound **1l** is best carried out with stirring for 30 min at −78 °C and an additional 2 h at −20 °C. The direct nitration suffers from the poor resistance of [2.2]paracyclophanes to oxidation and tendency to polymerization.[29] In contrast, the approach used herein via nitration under mild conditions in superacidic media was found to be an effective pathway toward compounds **1k** and **1l** as yields between 93 and 95% were detected.[27]

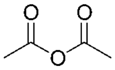
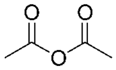
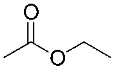
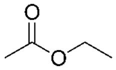
Scheme 1. Chemical Synthesis of Functionalized [2.2]Paracyclophanes Used as Precursor for CVD Polymerization

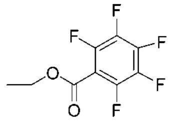
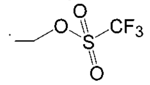


(***i***: $AlCl_3$, TFAA; ***ii***: aq. KOH, reflux; ***iii***: methanol, aq. HCl, reflux; ***iv***: pentafluorophenol trifluoroacetate, pyridine; ***v***: LAH, reflux; ***vi***: acetic acid anhydride, pyridine 130 °C; ***vii***: TFAA, O °C; ***viii***: triflic acid anhydride, methylene chloride, O °C, ***ix***: bis(dimethyl amino)naphthalene, trimethyloxonium tetrafluoroborate; ***x***: superacidic condition, HNO_3; ***xi***: triiron dodecacarbonyl, phase transfer conditions; ***xii***: Mg, propargylic bromide; ***xiii***: propargylic bromide, CuCl, ΔH; ***xiv***: acetylenedicarboxylic acid dimethylester, ΔH; ***xv***: anhyd. H_2SO_4; ***xvi***: $NaBH_4$).

Scheme 2. CVD Polymerization of Functionalized [2.2]Paracyclophanes To Yield the Corresponding Functionalized Poly(*p*-xylylenes)



#	R₁	R₂	R₃	R₄
2a	CH_2OH	H	H	H
2b	CH_2OCH_3	H	H	H
2c	CH_2OCOCH_3	H	H	H
2d	$COOCH_3$	H	H	H
2e	$COOCH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$
2f				
2g				
2h	NH_2	H	H	H

#	R₁	R₂	R₃	R₄
2i	NH_2	H	NH_2	H
2j		H	H	H
2k	CH_2OCOCF_3	H	H	H
2l	$COCF_3$	H	H	H
2m		H	H	H
2n	H	H	H	H

Subsequent reduction of the nitro[2.2]paracyclophanes to mono- and diamino[2.2]paracyclophane (**1m**−**1n**) was carried out with triiron dodecacarbonyl under toluene/aqueous KOH phase transfer conditions in the presence of 18-crown-6 as phase transfer catalyst.[27]

4,5,12,13-Tetrakis(methyloxycarbonyl)[2.2]paracyclophane (**1o**) was obtained by Diels−Alder reaction of acetylenedicarboxylic acid dimethyl ester with hexatetraene which was previously generated by the conversion of propargylic bromide with the Grignard compound allenylic magnesium bromide.[25] Dehydratization of **1o** with concentrated sulfuric acid resulted in [2.2]paracyclophane-4,5,12,13-tetracarboxylic acid dianydride (**1p**). [2.2]Paracyclophane-4,5,12,13-tetracarboxylic γ-butyryl lactone (**1q**) was then synthesized from compound **1p** by reduction with sodium borohydride.

CVD Polymerization. The CVD process followed a procedure first described by Gorham that was previously used to produce commercial, pinhole-free coatings.[30] As shown in Scheme 2, functionalized [2.2]paracyclophanes were pyrolyzed in the vapor phase to form the corresponding *p*-quinodimethanes, which condensed onto a substrate and spontaneously polymerized. Optimized polymerization conditions are summarized for each [2.2]paracyclophane in Table 1. Since the temperature of the substrate is relatively low (<25 °C), even temperature-sensitive substrates can be coated without affecting the substrate material. Carefully purified [2.2]paracyclophanes were sublimed under a reduced pressure and temperatures between 220 and 355 °C depending on the individual [2.2]paracyclophane. The sublimed material was then transferred to the pyrolysis zone and was exposed to temperatures between 600 and 750 °C using pressures between 0.07 and 0.2 mbar to ensure cleavage of the C−C bonds resulting in the corresponding *p*-quinodimethanes (monomers). In the last step, monomers polymerized on the substrate at temperatures below 25 °C. Exploitation of functionalized [2.2]paracyclophanes for CVD polymerization is generally limited by the requirement to preserve the integrity of the functional groups under the conditions of *p*-quinodimethane creation in the pyrolysis zone. CVD polymerization of a specific [2.2]paracyclophane required optimum adjustment of reaction conditions to minimize decomposition. Thus, the experimental setup[22] was designed to individually control several polymerization parameters, such as pyrolysis temperature, pressure, gas flow, substrate temperature, and temperature and heating rate of the sublimation zone. We found the pyrolysis temperature to be critical for the quality of the reactive coatings: For sensitive polymers such as esters, ketones, or triflates, pyrolysis was best conducted at temperatures under 670 °C as compared to 750 °C used for the unfunctionalized [2.2]paracyclophane. On the other hand, amine **1m** or lactone **1q** was deposited as homogeneous films with excellent properties at temperatures above 720 °C.

Argon was used as a carrier gas to dilute *p*-quinodimethane concentration in the gas phase. A delicate balance of argon flow rate and pressure was maintained, as an increase in flow rate at a constant pressure reduced the concentration of the precursor in the gas phase. This resulted in reduced intermolecular interactions and prohibited side reactions. On the other hand, higher pressure at a constant argon flow rate resulted in decreased sublimation and lower monomer concentrations in the gas phase. In this case, contact times of the [2.2]paracyclophanes were extended, resulting in enhanced cleavage of the C−C single bonds and enhanced tendency to decompose. Generally, moderately low pressures between 0.12 and 0.2 mbar were used to guarantee complete formation of *p*-quinodimethanes without favoring intermolecular interactions. However, if pyrolysis temperatures above 720 °C were chosen,

Table 2. Chemical Composition of Poly(*p*-xylylenes) Deposited by CVD Polymerization onto Gold Substrates As Examined by XPS and Grazing Angle IR Spectroscopy

	atomic ratios[a]	XPS signals	IR bands
2a	O/C: 5.9 (6.0)	285.0 (*C*−C); 286.3 (*C*−O); 291.5 ($\pi \to \pi^*$); 531.9 (C−*O*)	835, 892, 1025 (C−O), 1163, 1245, 1450, 2863, 2928, 3013, 3308 (OH) cm^{-1}
2b	O/C: 6.3 (5.6)	285.0 (*C*−C); 286.7 (*C*−O); 291.5 ($\pi \to \pi^*$); 531.0 (C−*O*)	830, 1030 (CO), 1265, 1362, 1378, 1930, 2873, 2940, 3017 cm^{-1}
2c	O/C: 12.2 (10.5)	285.0 (*C*−C); 286.5 (*C*−O); 289.6 (*C*═O); 291.7 ($\pi \to \pi^*$); 530.0 (C═*O*); 531.3 (C−*O*)	830, 1034, 1260, 1363, 1378, 1746 (C═O), 2863, 2935, 3018 cm^{-1}
2d	O/C: 15.9 (11.1)	285.0 (*C*-C); 286.0 (*C*-O); 289.5 (*C*═O); 291.7 ($\pi \to \pi^*$); 530.2 (C═*O*); 531.6 (C−*O*)	789, 817, 1076, 1112, 1209, 1260, 1276, 1434, 1726 (C═O), 2858, 2914, 2950, 3018 cm^{-1}
2e	O/C: 26.0 (33.3)	285.0 (*C*−C); 286.3 (*C*−O); 289.3 (*C*═O); 291.5 ($\pi \to \pi^*$); 529.9 (C═*O*); 531.3 (C−*O*)	798, 840, 1004, 1122, 1214, 1296, 1440, 1737 (C═O), 2879, 2945, 3001 cm^{-1}
2f	O/C: 26.4 (30.0)	285.0 (*C*−C); 286.2 (*C*−CO−O); 289.5 (*C*═O); 291.7 ($\pi \to \pi^*$); 532.5 (C═*O*); 533.9 (C−*O*)	763, 850, 917 (CO), 1132, 1188, 1260 (CC), 1452, 1501, 1778 (C═O), 1849 (C═O), 2863, 2930 cm^{-1}
2g	O/C: 19.5 (20.0)	285.0 (*C*−C); 285.7 (*C*−CO−O), 286.9 (*C*−O); 288.9 (*C*═O); 290.7 ($\pi \to \pi^*$); 531.5 (C═*O*); 533.0 (C-*O*)	846, 1035, 1076, 1161, 1364, 1450, 1501, 1762 (C═O), 2858, 2935 cm^{-1}
2h	N/C: 6.3 (6.3)	285.0 (*C*−C); 286.0 (*C*−N); 291.3 ($\pi \to \pi^*$); 397.1 (C−*N*)	820, 866, 1117, 1286, 1440, 1521, 1583, 1624, 2858, 2914, 3001, 3237 (NH), 3360 (NH), 3426 (NH) cm^{-1}
2i	N/C: 11.1 (12.5)	285.0 (*C*−C); 286.0 (*C*−N); 291.3 ($\pi \to \pi^*$); 397.1 (C−*N*)	820, 861, 1434, 1521, 1582, 1629, 2853, 2928, 3005, 3232 (NH), 3355 (NH), 3426 (NH) cm^{-1}
2j	O/C: 7.8 (8.7); F/C: 23.9 (21.8)	285.0 (*C*−C); 285.8 (*C*−CO−O); 286.7 (*C*−O); 288.3 (*C*═O); 290.6 (*C*−F); 292.2 ($\pi \to \pi^*$); 532.5 (C═*O*); 533.9 (C−*O*); 686.9 (C−*F*)	999 (CF), 1040 (CF), 1118 (CCO), 1182, 1250 (OCC), 1470, 1491, 1521, 1761 (C═O), 2858, 2930 cm^{-1}
2k	O/C: 7.3 (10.5); F/C: 17.8 (15.8)	285.0 (*C*−C); 285.5 (*C*−CO−O); 288.4 (*C*═O); 292.9 (*C*−F); 292.0 ($\pi \to \pi^*$); 530.9 (C═*O*); 534.0 (C−*O*); 686.8 (C−*F*)	822, 1048, 1145, 1178, 1225, 1414, 1467, 1498, 1785 (C═O), 2866, 2923, 3023 cm^{-1}
2l	O/C: 6.0 (5.5); F/C: 14.2 (16.6)	285.0 (*C*−C); 288.3 (*C*═O); 293.6 (*C*F$_3$); 530.5 (C═*O*); 687.0 (C−*F*)	822, 984, 1165, 1210, 1712 (C═O), 2862, 2926, 3015 cm^{-1}
2m	O/C: 16.9 (16.7); F/C: 18.2 (16.7); S/C: 3.4 (5.5)	168.0 (*S*(O$_2$)); 285.0 (*C*−C); 285.9 (*C*−O−S); 290.6 (*C*−F); 291.7 ($\pi \to \pi^*$); 532.0 (S═*O*); 688.0 (C−*F*)	646, 692, 758, 1030, 1163, 1235 (SO$_2$), 1286, 1496 (SO$_2$), 1537, 1609, 2853, 2925, 3078 cm^{-1}
2n		285.0 (*C*−C)	820, 1022, 1140, 1278, 1514, 1690, 2855, 2922, 3018 cm^{-1}

[a] Calculated XPS ratios in parentheses.

pressures could be as low as 0.05 mbar (for polymer **2g**). In addition, argon flow rates varied substantially between different polymers. Highest flow rates were used when high pyrolysis temperatures and moderate pressures were combined. For instance, alcohol **2a** was prepared with a pyrolysis temperature of 750 °C, a pressure of 0.08 mbar, and an argon flow rate as high as 10.0 sccm (standard cubic centimeter). In this case, the dilution effect of the carrier gas inhibited side reactions despite harsh pyrolysis conditions.

Polymer Characterization. Chemical compositions of the poly(*p*-xylylenes) were determined by X-ray photoelectron spectroscopy (XPS), microanalysis, and reflection−absorption infrared spectroscopy (RAIRS). As shown in Table 2, chemical compositions (XPS) expressed by molecular ratios O/C, N/C, F/C, and S/C were generally in good accordance with expected theoretical values. In some cases, however, both over- and under-determination of oxygen was determined by XPS. Polymers **2b**−**d** showed an increased amount of oxygen that may indicate oxidation during or after polymerization. In addition, secondary reactions of free oxygen with radicals of the chain ends may account at least partially for this finding. Similar reactions were observed for plasma-etched polymers, where free radicals were found to react with oxygen to yield hydroperoxides.[31] On the other hand, oxygen-rich polymers, such as esters **2e** and **2k** or anhydride **2f**, were characterized by slightly decreased oxygen contents. Partial decomposition of groups may account for these results. Similarly, a slight decrease in fluorine and sulfur content indicated partial loss of the triflate groups of polymer **2m** under the conditions of pyrolysis. For all polymers, the XPS spectra revealed binding energies that are in accordance with the expected chemical structures (Scheme 2). While these results confirmed the integrity of the functional groups during polymerization, no evidence was found to support the occurrence of broad side reactions. Occasionally, signals at binding energies around 291.5 eV were detected, which are typical for $\pi \to \pi^*$ transitions associated with aromatic polymers.

XPS results revealed the chemical composition of the polymer films to be in good accordance with the theoretically expected values. Gold signals were not detected in any of the polymer films. We concluded that all polymer films were homogeneously deposited without gaps or larger pinholes that would give raise to the detection of gold signals. XPS signals were generally acquired under a constant emission angle of 55°, which results in an information depth of about 6 nm. However, for polymer **2j**, XPS composition was studied at variable emission angles (15°−75°). Both O/C and F/C ratios did not change over the entire range, indicating a homogeneous distribution of the polymer in the studied bulk volume.

To support the XPS study, we determined the elemental bulk composition of the polymers **2a**−**2n** by microanalysis (cf. Table 3). XPS and elemental analysis are complementary methods in the sense that XPS allows selective study of the outermost surface volume, while microanalysis reveals information regarding the bulk composition. Similar to the XPS results, elemental compositions of polymers **2a**−**2n** determined by microanalysis were in excellent agreement with the calculated compositions. Furthermore, the results of the elemental analysis allowed further evaluation of the divergence in the elemental composition detected by XPS. Microanalysis did not confirm differences from the chemical composition determined by XPS. Conse-

Table 3. Elemental Composition of Poly(*p*-xylylenes) Deposited by CVD Polymerization onto Glass Substrates As Examined by Microanalysis

	experimental	theoretical	lit.
2a	C: 85.74; H:6.65; O: 3.57	C: 85.67; H: 7.61; O: 6.71	20
2b	C: 85.47; H: 8.23; O: 6.12	C: 85.67; H: 7.99; O: 6.34	
2c	C: 83.89; H: 6.87; O: 10.55	C: 81.40; H: 7.19; O: 11.41	
2d	C: 81.10; H: 6.78; O: 12.14	C: 81.17; H: 6.81; O: 12.01	
2e	C: 65.89; H: 5.45; O: 28.	C: 65.45; H: 5.49; O: 29.06	
2f	C: 68.97; H: 3.47; O: 26.57	C: 68.97; H: 3.47; O: 27.56	
2g	C: 74.92; H: 5.11; O: 17.86	C: 74.99; H: 5.03; O: 19.98	
2h	C: 81.37; H: 7.47; N: 8.34	C: 86.05; H: 7.67; N: 6.27	20
2i	C: 80.57 H: 7.52; N: 12.21	C: 80.63; H: 7.61; N: 11.75	
2j	C: 65.70; H: 3.59; F: 24.01; O: 7.89	C: 66.03; H: 3.61; F: 22.71; O: 7.65	
2k	C: 65.45; H: 4.32; F: 22.40; O: 6.48	C: 71.04; H: 4.97; F: 18.73; O: 5.26	20
2l	C: 69.11; H: 5.35; F: 16.03; O: 7.98	C: 68.26; H: 5.13; F: 17.05; O: 9.57	
2m	C: 64.37; H: 4.43; F: 13.24; O: 13.61; S: 6.37	C: 58.37; H: 4.63; F: 15.39; O: 12.96; S: 8.66	
2n	C: 92.24; H: 7.46	C: 92.26; H: 7.44	

quently, these superficial divergences must be restricted to the outermost molecular layers.

To examine the integrity of functional groups unambiguously, RAIRS was used as complementary surface analysis method. Especially when conducted under a grazing angle of 85°, RAIRS revealed surface-sensitive information regarding the presence or absence of functional groups. IR data are summarized in Table 2. For polymer **2a**, OH stretches were found at a wavelength of 3308 cm^{-1}, while polymers **2h** and **2i** were characterized by NH stretches at wavelengths of 3237 (**2i**: 3232), 3360 (**2i**: 3355), and 3426 cm^{-1}. These stretches confirm the presence of hydroxyl or amino groups, and in the case of polymers **2h** and **2i**, the characteristic pattern (double band) of the stretches indicated the presence of primary amino groups. Consequently, N-alkylation under the condition of pyrolysis was ruled out. The integrity of carboxyl or carbonyl groups was verified by the presence of $C{=}O$ valence stretches detected for polymers **2c** (1746 cm^{-1}), **2d** (1726 cm^{-1}), **2e** (1732 cm^{-1}), **2g** (1762 cm^{-1}), **2k** (1785 cm^{-1}), and **2l** (1712 cm^{-1}). Similarly, the IR spectrum of polymer **2j** confirmed the integrity of the pentafluorophenol ester group as indicated by a characteristic signal at a wavelength of 1761 cm^{-1} ($C{=}O$) and supported by characteristic bands of $C-F$ stretching vibrations at wavelengths between 999 and 1040 cm^{-1}. Furthermore, $C-C-O$ and $O-C-C$ stretches were found at wavelengths of 1118 and 1250 cm^{-1}, respectively. Polymer **2f** was characterized by the double signal of the $C{=}O$ stretching vibration at 1778 and 1849 cm^{-1}, which revealed the typical intensity distribution of cyclic anhydrides with the stretch at 1778 cm^{-1} being of higher intensity. Furthermore, characteristic bands of $C-O$ and $C-C$ stretching vibrations at wavelengths of 917 and 1260 cm^{-1} accordingly confirmed the presence of unsaturated cyclic anhydride groups. The IR spectrum of polymer **2b** revealed aliphatic $C-O$ stretches at wavelengths of 1030 cm^{-1} and confirmed the presence of the methoxy group, while the IR spectrum of polymer **2m** is characterized by the symmetric and asymmetric SO_2 stretches at wavelengths of 1235 and 1496 cm^{-1}.

In summary, the repertoire of complementary analytical methods used in this study allowed us to confirm the chemical composition of all 13 poly(*p*-xylylenes). CVD polymerization of [2.2]paracyclophanes resulted in transparent and topologically uniform polymer films. Film thickness varied substantially as films deposited in this study were between 50 and 781 nm thick (cf. Table 4). The film thickness is mainly determined by the amount of starting material used for polymerization, although the heating rate of the sublimation zone influenced the film thickness as well.

Optical Properties of the Polymer Films. Several members of the poly(*p*-xylylene) family including poly(*p*-xylylene), poly(chloro-*p*-xylylene), or poly(tetrafluoro-*p*-xylylene) are optically anisotropic polymers and show optical birefringence.[32] The polymer chains are aligned in a preferred orientation and exhibit strong anisotropic molecular polarizibility due to their main-chain phenyl groups. Benzene is a planar molecule with a delocalized π-electron system that has an anisotropic molecular polarizibility of $\Delta\alpha = 5.62$ Å^3.[33] Substitution of the benzene rings in the main chain of polymers **2a**−**q** alters the electronic properties and changes the anisotropic molecular polarizibility. Therefore, the electronic nature of the functional groups must be expected to directly influence the optical properties of the polymer films. Other critical parameters include the reflection of chain orientation and the polymer crystallization. In this study, polymer films were examined as-deposited without optimizing deposition conditions with respect to optical properties or annealing samples after deposition.

Table 4. Optical Parameters of the Functionalized Poly(*p*-xylylenes) As Determined by Spectroscopic Ellipsometry at a Wavelength of 633 nm

				in-plane		out-of-plane		
functionality		RSE	film thickness (Å)	n_0	n_e	n_0	n_e	B
alcohol	**2a**	11.830	5121.4	1.4984	1.4512	1.4734	1.4168	0.0344
methyl ether	**2b**	5.410	418.4	1.5161	1.4649	1.4627	1.4307	0.0342
acetate	**2c**	12.932	2498.4	1.5657	1.4293	1.4275	1.3651	0.0642
methyl ester	**2d**	19.740	5181.5	1.4900	1.4307	1.4418	1.4052	0.0255
tetramethyl ester	**2e**	9.062	5943.7	1.5727	1.5065	1.5582	1.5328	−0.0263
anhydride	**2f**	2.421	557.2	1.6585	1.4565	1.5363	1.5329	−0.0764
lactone	**2g**	8.560	711.2	1.6176	1.3726	1.5145	1.4414	−0.0688
amine	**2h**	11.380	7808.0	1.5539	1.4616	1.5356	1.5153	−0.0537
diamine	**2i**	19.519	7247.5	1.4496	1.4162	1.4358	1.4038	0.0126
pentafluorophenol ester	**2j**	3.764	2806.4	1.4927	1.4355	1.4893	1.4458	−0.0103
trifluoroacetate	**2k**	2.472	497.3	1.6173	1.5039	1.5719	1.5003	0.0036
triflluoromethyl ketone	**2l**	10.030	3895.5	1.4544	1.4539	1.4841	1.4602	−0.0063
triflate	**2m**	4.603	208.2	1.5106	1.4515	1.7741	1.4802	−0.0451

Refractive indices were determined using a variable angle spectroscopic ellipsometer. The ellipsometric constants ψ and δ were measured vs wavelengths for three angles of incidence (65°, 70°, 75°). Then, experimental data were compared to data generated using a birefringent Cauchy dispersion model and showed excellent correlation with low root-mean-square errors (RSE, see Table 3). Since all polymer films were well described by assuming uniaxial properties, both extraordinary and ordinary indices of refraction are listed in Table 4 for a wavelength of 633 nm. Refractive indices n_0 varied between 1.4544 (**2l**) and 1.6585 (**2f**), while the extraordinary indices of refraction (n_e) diverged from 1.3726 (**2g**) to 1.5065 (**2e**). All polymer films were negatively uniaxial ($n_e < n_0$) with the optic axis parallel to the substrate surface.

With respect to applications in optical devices or waveguides, another critical property is the optical birefringence of a material. Optical birefringence can be immediately determined from refractive indices as follows:[34]

$$B = \Delta n_e = n_{\text{in-plane}} - n_{\text{out-of-plane}} \qquad (1)$$

with $n_{\text{out-of-plane}}$ being the out-of-plane index of refraction (perpendicular to the plane of substrate) and $n_{\text{in-plane}}$ being the in-plane index of refraction (defined by the plane of substrate). The polymer films examined in this study showed a relatively wide range of birefringence due to the variable electronic properties of the prepared polymers. Interestingly, some of the fluorinated polymers (**2j**−**l**) showed extremely low birefringence (abs(B) < 0.01). In contrast, highest values of optical birefringence were found for polymers **2c**, **2f**, and **2g** (abs(B) > 0.06). Although two members of this group, anhydride **2f** and lactone **2g** were 4-fold-substituted, a simple correlation between high optical birefringence and high substitution degree is not evident since the comparably substituted tetramethyl ester **2e** showed rather moderate birefringence (−0.0263). The optical properties reported in Table 4 depended on the chemical nature of the functional groups and confirmed the assumption that design of functionalized polymers may be an appropriate approach to control optical properties. However, other critical parameters such as deposition temperature or postdeposition annealing critically influence the optical properties of polymers as well and may be used to enhance structure-based tendencies.

Conclusions

Functionalized poly(p-xylylenes) have recently gained interest as thin-layer coatings. The overall impact of this technology in surface engineering may depend on how variable poly(p-xylylenes) with different functional groups can be prepared enabling different binding modes for attachment of biomolecules. In this study, we broadened the platform of functionalized polymers that can be prepared by CVD polymerization. The synthesis of functionalized [2.2]paracyclophanes and the subsequent polymerization resulted in 13 different polymers with distinct chemical and optical properties. The approach may also assist in assessing structure−function relationships for poly(p-xylylenes) or similar polymer families. In summary, this study extends the applicability of CVD polymerization since a suitable candidate can now be chosen among a diverse group of polymers, and by optimizing the preparation conditions, the polymer can be tailored to the specific requirements of a given application.

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