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Partial and Complete Chemical Modification of Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) by Addition of Dichloroketene

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ABSTRACT: Dichloroketene, generated by the ultrasound-promoted dechlorination reaction of trichloroacetyl chloride with zinc, has been added to the carbon–carbon double bonds of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (poly-I). The molecular weight distribution of the adduct polymer poly[[(2,2-dichloro-1-oxo-3,4-cyclobutanediyl)-*cis*-bis(methylene)](methylphenylsilylene)] [poly(I–Cl_2C=C=O)] has been characterized by gel permeation chromatography (GPC). The polymer microstructure has been elucidated by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. Likewise, a series of random copolymers has been prepared in which only some of the carbon–carbon double bonds of poly-I have been reacted with dichloroketene. The molecular weight distributions of these copolymers have been determined by GPC. These have been characterized spectroscopically as above. The glass transition temperatures (T_g's) of these copolymers, as well as that of the 100% adduct homopolymer above, have been determined by differential scanning calorimetry (DSC). They are found to increase linearly with the percent of carbon–carbon double bonds that have reacted with dichloroketene.

Introduction

Dichloroketene (II) is known to react with the C–C double bonds of alkenes of yield 2,2-dichlorocyclobutanones in high yield via [2 + 2] cycloaddition reactions.[1] Unlike less reactive ketenes, II reacts readily even at room temperature with the C–C double bonds of unactivated alkenes, such as cyclopentene and cyclohexene.[2] These [2 + 2] cycloaddition reactions proceed stereospecifically[3] via a concerted [$_\pi 2_s$ + $_\pi 2_a$] reaction path in which the π-system of the alkene and the C–C double bond of the ketene approach each other via an orthogonal transition state.[4] Even when a [2 + 4] cycloaddition pathway is possible, [2 + 2] cycloadducts are formed.[5–7]

The facile generation of II by either the homogeneous dehydrohalogenation reaction of dichloroacetyl chloride with triethylamine or the heterogeneous dechlorination reaction of trichloroacetyl chloride with activated zinc makes these [2 + 2] cycloaddition reactions the most direct procedure to prepare 2,2-dichlorocyclobutanones. The recent observation that ultrasound promotes this heterogeneous reaction with zinc further facilitates the preparation of 2,2-dichlorocyclobutanones.[8] This probably results from the well-known activating effect of ultrasound on metal surfaces.[9]

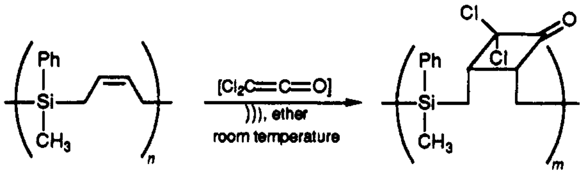
2,2-Dichlorocyclobutanones are themselves versatile synthetic intermediates that can easily be converted to cyclobutanones by metal reduction (Zn/H^+) of the carbonyl-activated C–Cl bonds. They can also be modified under basic conditions to yield cyclopropanecarboxylic acids.[10,11]

One example of addition of II to the C–C double bond of an allylic silane has been reported. This involves the reaction of one of the C–C double bonds of 5-(trimethylsilyl)cyclopentadiene with II to yield 7,7-dichloro-4-*exo*-(trimethylsilyl)bicyclo[3.2.0]hept-2-en-6-one.[12,13]

Despite the reactivity of II, no examples of its addition to the C–C double bonds of unsaturated polymers such as 1,4-polybutadiene or polyisoprene have been reported. This is surprising since there is considerable interest in the chemical modification of polymers.[14–17]

Results and Discussion

We should like to report the addition of II to the C–C double bonds of poly-I to yield the adduct polymer poly[[(2,2-dichloro-1-oxo-3,4-cyclobutanediyl)-*cis*-bis(methylene](methylphenylsilylene)] [poly(I–Cl_2C=C=O)]. This reaction was carried out under heterogeneous conditions by addition of trichloroacetyl chloride to a solution of poly-I in diethyl ether containing zinc powder under the influence of ultrasound.



poly-I

poly(I–Cl_2C=C=O)

These experimental conditions are less than ideal. Ultrasound is well-known to degrade the molecular weight of high polymers.[18–21] In control experiments, we have shown that the molecular weight distributions of both poly-I and poly(I–Cl_2C=C=O) are, in fact, decreased by treatment with ultrasound in the absence of either zinc or trichloroacetyl chloride. Further, dechlorination of trichloroacetyl chloride by zinc yields not only II but also zinc chloride, a Lewis acid. In control experiments, we have demonstrated that the molecular weight of poly-I decreases on treatment with zinc chloride in ether in the absence of ultrasound. On the other hand, treatment of poly(I–Cl_2C=C=O) with zinc chloride resulted in little degradation of the polymer. Polymer degradation under the reaction conditions may be caused not only by zinc chloride but also by the strong acid $H^+(ZnCl_3)^-$. Allylic Si–C bonds are known to undergo electrophilic cleavage on treatment with Brønsted acids.[22] While we have carefully dried all equipment and reagents, the complete elimination of water is probably impossible. Trichloroacetyl chloride will certainly react with any traces of water to yield hydrochloric acid, which, in turn, will complex with zinc chloride to yield $H^+(ZnCl_3)^-$.[23] We have attempted to eliminate this problem by addition of pyridine to the heterogenous

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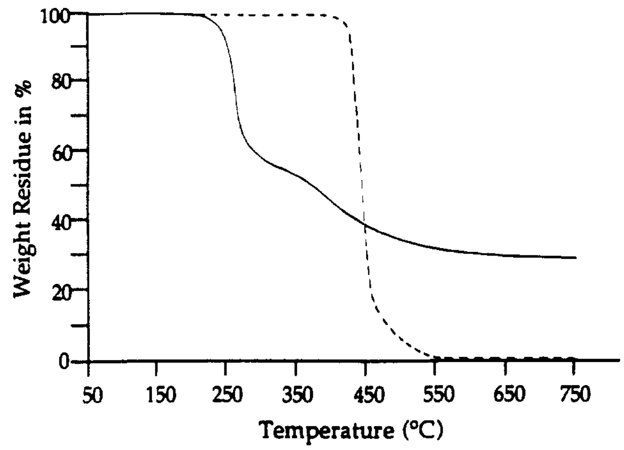


Figure 1. TGA of poly-I and poly(I-$Cl_2C{=}C{=}O$).

reaction media. Under these conditions, no addition of II to the C–C double bonds of poly-I was observed. The negative effect of pyridine on the reaction may result from the formation of (trichloroacetyl)pyridinium chloride or may be due to the formation of a pyridine complex with zinc chloride.[24,25] Lewis acid catalysis by zinc chloride may, in fact, be necessary to achieve the [2 + 2] cycloaddition reaction of II with the C–C double bonds of poly-I.

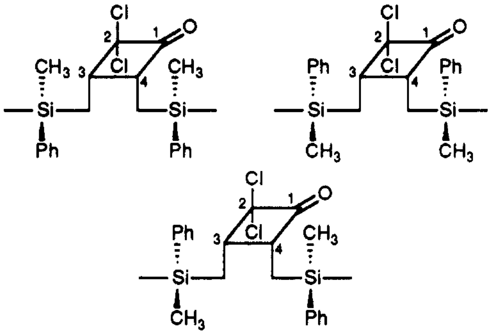
Consideration of these problems led us to attempt to carry out the addition of II to the C–C double bonds of poly-I under homogeneous conditions by reaction of dichloroacetyl chloride with triethylamine. This alternative procedure led to **very low** molecular weight poly(I-$Cl_2C{=}C{=}O$). The source of this polymer degradation reaction is not understood. In control experiments, neither triethylamine nor triethylamine hydrochloride caused major decreases in the molecular weight of poly-I.

For these reasons, we have utilized the heterogeneous reaction of trichloroacetyl chloride and zinc to generate II. We have carefully chosen the experimental parameters to achieve the highest molecular weight poly(I-$Cl_2C{=}C{=}O$). Specifically, the reaction time has been minimized to diminish the cleavage of polymer by ultrasound. Zinc powder in ether was activated by treatment with ultrasound prior to the addition of poly-I, which permits the immediate generation of II on addition of trichloroacetyl chloride. Nevertheless, to achieve complete chemical modification of poly-I requires the generation of II in large (800%) excess. These conditions expose the remaining allylic Si–C linkages in the partially chemically modified polymer to large excesses of zinc chloride. The result is that as the extent of chemical modification increases, the molecular weight of poly(I-$Cl_2C{=}C{=}O$) decreases.

These observations are surprising since reaction of 5-(trimethylsilyl)cyclopentadiene with a stoichiometric amount of II, generated under homogeneous conditions, leads to a 70% yield of dichloroketene adduct.[5,6]

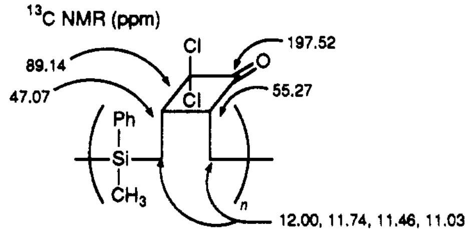
The thermal stability of poly(I-$Cl_2C{=}C{=}O$) in a nitrogen atmosphere has been determined by thermal gravimetric analysis (TGA) (Figure 1). Poly(I-$Cl_2C{=}C{=}O$) is less thermally stable than poly-I (Figure 1). Poly(I-$Cl_2C{=}C{=}O$) is stable to 170 °C. Between 170 and 210 °C 10% of the initial sample weight is lost. Rapid weight loss (33%) occurs between 210 and 260 °C. Slower weight loss (10%) occurs between 260 and 375 °C. Ten percent weight is lost between 375 and 440 °C. Finally, between 450 and 575 °C 7% weight loss occurs. A dark purple residue amounting to 30% is stable to 750 °C.

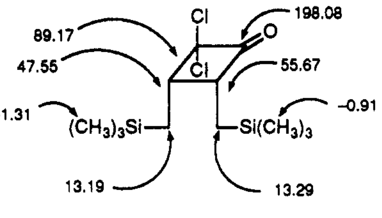
The microstructure of the poly(I-$Cl_2C{=}C{=}O$) is quite complex. The NMR spectra of the (2,2-dichloro-1-oxo-3,4-cyclobutanediyl)-*cis*-bis(methylene) (III) units can be considered on the basis of a diad analysis, in which the neighboring methylphenylsilylene (IV) units can be either cis or trans to one another. This leads to a prediction of three types of microenvironments.



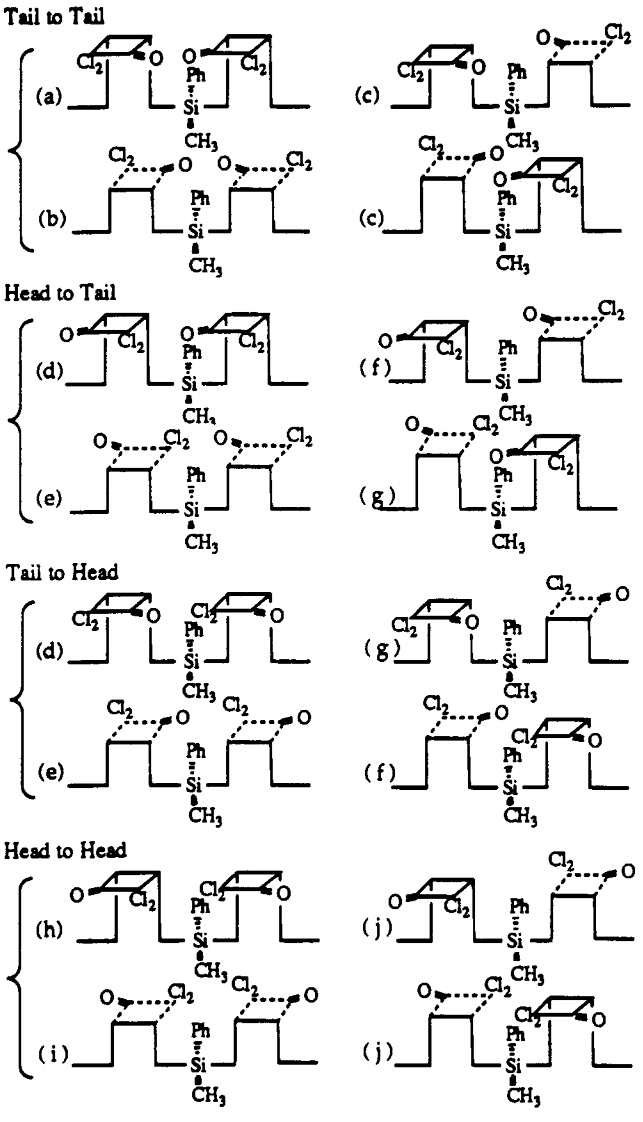
These differences are not seen in the ^1H NMR. The broad singlet centered at 2.94 ppm is assigned to the methine hydrogen bonded to C_3, while the resonance centered at 3.40 ppm is assigned to the methine hydrogen bonded to C_4 of the 2,2-dichlorocyclobutanone rings. These assignments are based on the ^1H NMR spectrum of 2,2-dichloro-*cis*-3,4-bis[(trimethylsilyl)methyl]cyclobutanone.[26] This model compound was prepared by the addition of II to 1,4-bis(trimethylsilyl)-*cis*-2-butene.[27]

Likewise, only single resonances are observed in the ^{13}C NMR for the carbonyl carbon (197.52 ppm) and the 2,2-dichloro-substituted carbon (89.14 ppm) as well as for methine C_3 (47.07 ppm) and methine C_4 (55.27 ppm). On the other hand, four resonances due to the methylene carbons are observed (12.00, 11.74, 11.46, 11.03 ppm) as predicted by this diad model.





The NMR spectra of the IV units also have been analyzed on the basis of a diad analysis. There are 10 possible arrangements of adjacent III units about a particular IV unit. This results from two stereochemical considerations. First, the IV units can be bonded to a methylene carbon which is attached to either C_3 or C_4 of the 2,2-dichlorocyclobutanone ring. If IV is bonded to the methylene group attached to C_3, it is remote from the carbonyl group of the 2,2-dichlorocyclobutanone ring. On the other hand, if IV is bonded to the methylene group attached to C_4, it is proximate to the carbonyl group of the 2,2-dichlorocyclobutanone ring. This leads to four arrangements of adjacent 2,2-dichlorocyclobutanone rings to one another: tail to tail, head to tail, tail to head, and head to head. In turn, these are further differentiated since adjacent 2,2-dichlorocyclobutanone rings can either



a : b : c : d : e : f : g : h : i : j
= 0.5 : 0.5 : 1.0 : 1.0 : 1.0 : 1.0 : 1.0 : 0.5 : 0.5 : 1.0

Figure 2. Diad microstructure analysis of methylphenylsilylene units of poly(I–Cl_2C=C=O).

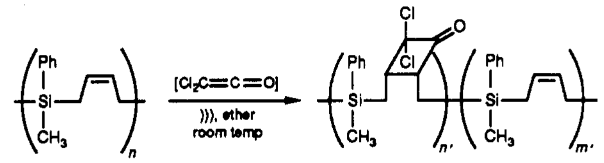
be syn or anti to one another, that is, on the same or opposite sides of the polymer chain. These possible microstructures are illustrated in Figure 2.

This diad analysis predicts 10 different microenvironments for the IV groups in a ratio of 0.5:0.5:1.0:1.0:1.0:1.0:1.0:0.5:0.5:1.0. In fact, nine distinct ^{13}C NMR resonances at −3.43, −3.59, −3.87, −4.10, −4.33, −4.29, −4.74, −4.97, and −5.23 ppm in a ratio of 0.5:1.0:0.5:1.0:1.0:2.0:0.5:1.0:0.5 are observed for the methyl groups bonded to silicon in poly(I–Cl_2C=C=O). This is in remarkable agreement with the prediction of the diad model. Apparently, two of the lines whose relative intensity are 1.0 fortuitously overlap. Likewise, the ipso carbon of the phenyl group is sensitive to differences in microenvironment. A broad multiplet comprised of eight overlapping lines is seen between 134.94 and 135.59 ppm. On the other hand, single broad lines are observed for the ortho 133.87, meta 128.18, and para 129.86 ppm carbons. Apparently, these are sufficiently remote that they are not sensitive to differences in microenvironment. A broad peak that results from the overlap of nine resonances between −3.74 and −2.10 ppm is observed in the ^{29}Si NMR for the silyl center of the IV units.

Table I
Effect of the Molar Ratio of Trichloroacetyl Chloride and Zinc with Respect to Poly-I on the Percent Composition of Copolymers, M_w/M_n, Yield, and Glass Transition Temperature

ratio Cl_3CCOCl	ratio Zn	% comp[a]	$M_w/M_n \times 10^{-3}$	yield, %	T_g, °C
0	0	0	130/75		−14.9
1	2	19	76/25	84	−4.1
6	10	40	40/22	79	17.0
8	12	55	28/18	74	33.1
8	15	80	25/17	69	46.8
8	20	100	12/8	65	60.4

[a] Percent composition = $n'/(n' + m')$



(I–Cl_2C=C=O   I

A series of copolymers has been prepared by less than stoichiometric reaction of II with the C–C double bonds of poly-I (Table I). These random copolymers have both 1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene (I) and [(2,2-dichloro-1-oxo-3,4-cyclobutanediyl)-*cis*-bis(methylene)]-(methylphenylsilylene) (I–Cl_2C=C=O) units. The ratio of these units in the copolymers can be determined easily from the ^1H NMR by integration of the resonances due to the phenyl groups bonded to silicon, which are present in both I and I–Cl_2C=C=O, compared to the resonance at 5.31 ppm due to the vinyl hydrogens of I.

The microstructures of these copolymers have been partially determined by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The IV units in copolymers can have either 1,4-*cis*-2-butene (V) or III units as nearest neighbors. This leads to a prediction of 15 possible microenvironments. At a very low level of chemical modification, many of the IV units will have V units on either side. These will have spectra identical with that of poly-I. At high levels of chemical modification, the spectra of the IV groups are essentially that of poly(I–Cl_2C=C=O), which had 10 possible microstructures as discussed above. At intermediate conversions, some of the IV units will be in an unsymmetrical environment in which a V unit is on one side and a III unit on the other. In these cases, IV may be bonded to the methylene group that is attached to either C_3 or C_4 of the 2,2-dichlorocyclobutanone ring. In the first case, IV is remote from the carbonyl group of the 2,2-dichlorocyclobutanone ring, while in the latter it is close to it. Furthermore, the 2,2-dichlorocyclobutanone rings can be on one or the other side of the polymer chain. This leads to a total of four distinct stereochemical microenvironments. In fact, in the ^1H NMR three signals are observed at 0.37, 0.30, and 0.25 ppm in a 1:1:2 intensity ratio for the hydrogens of the methyl group bonded to silicon rather than the four signals expected. Apparently, there is an accidental overlap of two of the methyl hydrogen signals at 0.25 ppm. None of the other signals in the ^1H NMR spectra are sensitive to differences in the microenvironment. In the ^{13}C NMR, four resonances assigned to methyl carbons bonded to silicon in such unsymmetrical environments are observed: −4.47, −4.52, −4.93, and −5.14 ppm in a 1:1:1:1 ratio as predicted. The ipso, meta, and para aromatic carbons of the IV units are likewise sensitive to differences in the microenvironment. Two sets of four unique ^{13}C NMR resonances are observed: 127.62, 127.83, 127.94, 128.18 and 128.96, 129.32, 129.43, 129.86 ppm. The former are assigned to the meta carbons of the IV unit, while the latter result from the para carbon. Three resonances at 137.77, 136.35, and 136.67 ppm are assigned

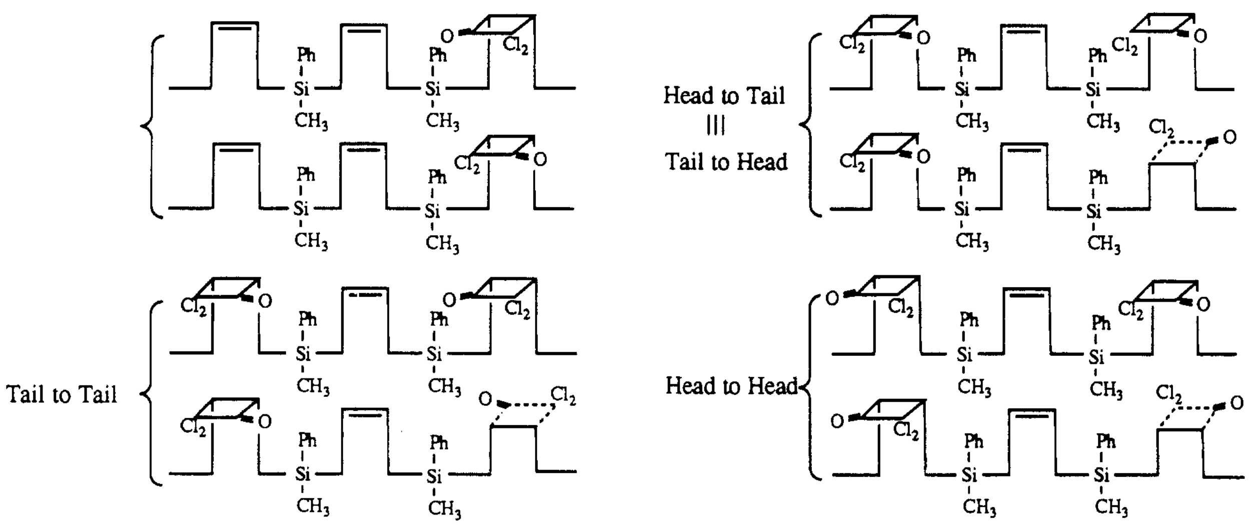


Figure 3. Triad microstructure analysis of 1,4-*cis*-2-butene units of copolymers composed of I–$Cl_2C{=}C{=}O$ and I groups.

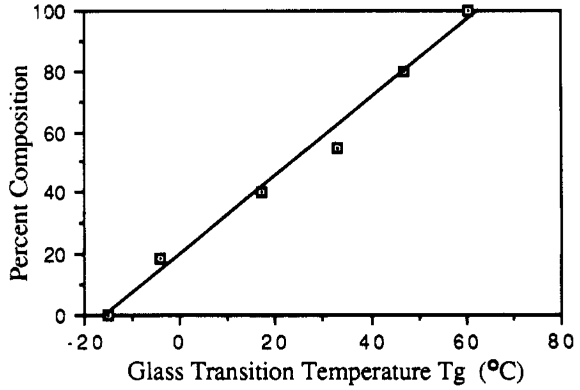


Figure 4. Effect of copolymer composition on glass transition temperature.

to the ipso carbon. Apparently, again two of these signals fortuitously overlap. Surprisingly, only a single signal (133.83 ppm) is observed for the ortho carbons.

The ^{29}Si NMR can likewise be understood in terms of this diad analysis. Two broad signals are observed: −3.3 to −3.4 and −3.7 to −3.9 ppm in a one to one ratio. The lower field signal results from IV units that are bonded to a methylene group attached to the C_4 of the 2,2-dichlorocyclobutanone ring. This places the carbonyl group in close proximity to IV. The agreement between the ^{1}H, ^{13}C, and ^{29}Si NMR spectra observed and those predicted by the unsymmetrical diad model is remarkably good.

Similarly, the vinyl carbons of V units are sensitive to the microenvironment. At low conversions, the chemical shift of the vinyl carbons of V units is identical with that of poly-I. At higher conversions three broad multiplets are observed: 122.48, 123.23, and 123.98 ppm. The last is comprised of four overlapping equal intensity lines at 123.85, 123.92, 124.04, and 124.13 ppm. These three multiplets may be accounted for in terms of a triad analysis outlined below. The resonances centered at 123.98 ppm may arise from vinyl carbons close to the carbonyl carbon of an adjacent 2,2-dichlorocyclobutanone ring, while the resonances centered at 122.48 ppm result from vinyl carbons that are remote from the carbonyl carbon of the adjacent 2,2-dichlorocyclobutanone ring. Finally, the central multiplet centered at 123.23 ppm arises from vinyl carbons that have V units as their neighbors. The methylene carbons are not sensitive to the detailed microstructure. Two groups of methylene carbons are observed. The first is centered at 15.5 ppm, while the second is observed at 11.6 ppm. The first is due to allylic carbons, while the second results from methylene carbons bonded to the C_3 and C_4 positions of 2,2-dichlorocyclobutanone rings (Figure 3).

The glass transition temperatures of the copolymers have been determined by DSC. A linear relationship has been found between the extent of chemical modification and T_g (Figure 4 and Table I). Such linear relationships between polymer properties and copolymer composition have been observed previously.[28,29]

Experimental Section

^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained on either a Bruker AM-360 or an IBM Bruker WP-270-SY spectrometer operating in the Fourier transform (FT) mode. Polymer solutions (5% w/v) in $CDCl_3$ were utilized to obtain ^{1}H NMR spectra. Twenty percent w/v solutions were used for the ^{13}C and ^{29}Si NMR spectra. ^{13}C NMR spectra were run with broad-band proton decoupling. Chloroform was used as an internal standard for ^{1}H and ^{13}C NMR spectra. A DEPT pulse sequence[30] or a NONOE sequence[31] with a pulse delay of 20 s was used to obtain ^{29}Si NMR spectra. These were externally referenced to TMS. FT IR spectra were obtained on an IBM FT IR/30S, DTAGS/CSI spectrometer. These were taken on films on NaCl plates.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers 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 Waters 7.8 mm × 30 cm, 10-μm particle size, mixed pore size, cross-linked polystyrene gel column was used for the separation. The elution solvent was HPLC grade THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 212 400, 110 000, 20 400, 4800, and 1350, whose M_w/M_n values are less than 1.09.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 50 °C for 10 min followed by an increase of 4 °C/min to 750 °C. Glass transition temperatures (T_g's) of polymers were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). Temperature scans where begun at −100 °C. After equilibration, the temperature was increased at a heating rate of 20 °C/min to 100 °C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl immediately prior to use. Zinc powder (Mallinckrodt, 325 mesh) and zinc chloride were dried under vacuum at 100 °C immediately prior to use. Trichloroacetyl chloride and dichloroacetyl chloride (Aldrich) were fractionally redistilled prior to use. All reactions were conducted under an atmosphere of purified argon and glassware was flame-dried under a nitrogen atmosphere.

Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (Poly-I). Poly-I (M_w/M_n = 130 000/75 000) was prepared by the anionic ring-opening polymerization of 1-methyl-1-phenyl-1-silacyclopent-3-ene[32] cocatalyzed by *n*-butyllithium and HMPA in THF at −78 °C. The polymer had properties in agreement with literature values.[33,34]

Addition of II to Poly-I. A 100-mL three-neck round-bottom flask was fitted with a reflux condenser, a pressure-equalizing addition funnel, and a 0.5-in. ultrasound probe, which was connected to a Tekmar 500W, 20-kHz, high-intensity ultrasonic generator. The ultrasound probe was sealed to the reaction flask with a rubber septum. Zinc powder (Table I) and diethyl ether (60 mL) were placed in the flask. The flask was placed in a water bath. This served to moderate the reaction temperature. The mixture was sonicated for 10 min at a 40% duty cycle at a 20% energy output. Poly-I (M_w/M_n = 130 000/75 000, 100 mg, 0.58 mmol) was added to the flask. Trichloroacetyl chloride (Table I) dissolved in 15 mL of diethyl ether was placed in the addition funnel. The reaction mixture was sonicated as above, while the solution of trichloroacetyl chloride was added dropwise to the reaction mixture over 30 min. The ultrasonic activation was continued for 10 min after completion of the addition. The ether solution was decanted from the excess zinc and zinc chloride salts. It was washed with water (3 × 50 mL) and then with aqueous sodium bicarbonate until the aqueous phase was no longer acidic. The ether solution was washed with an equal volume of saturated sodium chloride solution. The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered and the ether solvent was removed by evaporation under reduced pressure. The dichloroketene product polymer was dissolved in a minimum amount of THF and was purified by precipitation from methanol. This purification process was repeated. The product polymer was dried under vacuum for 24 h. Yields between 60% and 85% (Table I) were obtained. The lower the molecular weight of the product copolymer, the lower the yield. This may be due to incomplete precipitation of low molecular weight fractions. Spectral properties of poly(I-Cl$_2$C=C=O): ^{1}H NMR δ 0.29–0.43 (br m, 3 H), 0.9–1.3 (br m, 4 H), 2.9–3.1 (br s, 1 H), 3.35–3.5 (br s, 1 H), 7.24–7.34 (br s, 5 H); IR ν 3070, 3050, 3002, 2957, 2926, 1800 (s), 1428, 1257, 1191, 1143, 1114, 939, 910, 851, 817, 736, 700, 532 cm^{-1}. Elemental Anal. Calcd for 100% poly(I-Cl$_2$C=C=O), $C_{13}H_{14}SiCl_2O$: C, 54.74; H, 4.95; Cl, 24.86. Found: C, 54.95; H, 5.26; Cl, 25.00.

Reaction of Poly-I with II and Pyridine. Poly-I (M_w/M_n = 249 000/92 600, 100 mg, 0.58 mmol), Zn powder (0.57 g, 8.7 mmol), pyridine (0.47 mL, 5.75 mmol), and diethyl ether (40 mL) were placed in a three-neck round-bottom flask equipped with a 0.5-in. ultrasound horn as above. Sonication was begun and trichloroacetyl chloride (0.64 m L, 5.75 mmol) dissolved in diethyl ether (15 mL) was added slowly (0.5 h). The reaction mixture was sonicated for a total of 2 h. A 92% yield of poly-I was recovered, M_w/M_n = 37 500/17 500. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of recovered poly-I were identical with those of poly-I. The decrease in molecular weight of poly-I in this experiment may result from the effect of ultrasound.

Treatment of Poly-I with Ultrasound. Poly-I (M_w/M_n = 130 000/75 000, 80 mg, 0.44 mmol) and diethyl ether (50 mL) were placed in a 100-mL round-bottom flask equipped with an ultrasonic probe as above except that a rubber septum was utilized in place of the addition funnel. The solution was sonicated at a 40% duty cycle at a 25% energy output. After 1 h, sonication was momentarily stopped while a 3-mL aliquot was removed by syringe. The ether solvent was removed from this sample by evaporation under reduced pressure. Poly-I was dissolved in 1 mL of THF and was analyzed by GPC. After 1 h sonication the molecular weight of poly-I had decreased M_w/M_n = 77 700/37 200. Sonication of the solution was continued for an additional hour. GPC analysis at this time indicated a further decrease in the molecular weight of poly-I, M_w/M_n = 40 200/26 000.

Treatment of a Copolymer Composed of 60% I-Cl$_2$C=C=O and 40% I Units with Ultrasound. A copolymer composed of 60% I-Cl$_2$C=C=O and 40% I units (90 mg, 0.37 mmol), M_w/M_n = 30 000/12 500, and THF (40 mL) were placed in a 100-mL round-bottom flask equipped with an ultrasound probe as above. The solution was sonicated at a 40% duty cycle at a 25% energy output for 1 h. The polymer was purified by precipitation from methanol. GPC analysis of the molecular weight distribution of this recovered polymer gave M_w/M_n = 9950/7400.

Reaction of Poly-I with Zinc Chloride. In a 100-mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed diethyl ether (40 mL), poly-I (M_w/M_n = 144 000/118 000, 20 mg, 0.11 mmol), and zinc chloride (47 mg, 0.34 mmol). The reaction mixture was stirred for 12 h. The ether solution was decanted from the zinc chloride salts. Diethyl ether was removed by evaporation under reduced pressure. The molecular weight of recovered poly-I had significantly decreased M_w/M_n = 46 000/35 500. However, the ^{1}H NMR of recovered poly-I was identical with that of poly-I.

Reaction of Poly(I-Cl$_2$C=C=O) with Zinc Chloride. A reaction between 100% poly(I-Cl$_2$C=C=O) (M_w/M_n = 9500/7600, 20 mg, 0.07 mmol) and zinc chloride (29 mg, 0.21 mol) in diethyl ether (40 mL) was carried out with magnetic stirring for 12 h as above. After workup, the ^{1}H NMR of the recovered polymer was identical with that of the starting polymer. The molecular weight of recovered 100% poly(I-Cl$_2$C=C=O) had decreased slightly, M_w/M_n = 8100/6600.

Reaction of Poly-I with Dichloroacetyl Chloride and Triethylamine. In a 100-mL two-neck round-bottom flask equipped with a reflux condenser, a pressure equalizing addition funnel, and a Teflon-covered magnetic stirring bar were placed diethyl ether (50 mL), poly-I (M_w/M_n = 278 000/117 000, 100 mg, 0.58 mmol), and triethylamine (0.58 mL, 4.13 mmol). The flask was placed in an ice/water bath to maintain the reaction temperature at 0 °C. Dichloroacetyl chloride (0.33 mL, 3.48 mmol) dissolved in diethyl ether (15 mL) was placed in the addition funnel and this solution was added dropwise to the well-stirred reaction mixture over 30 min. The reaction mixture was stirred and allowed to warm to room temperature over 3 h. The ether solution was transferred to a separatory funnel and was washed with water (3 × 50 mL) and then with saturated aqueous ammonium chloride solution. Finally, the ether solution was washed with saturated aqueous sodium chloride. It was separated, dried over anhydrous magnesium sulfate, and filtered and the ether solvent removed by evaporation under reduced pressure. The product polymer was dissolved in a minimum amount of THF and was purified by precipitation from methanol. This process was repeated. The polymer was dried under vacuum for 24 h. In this way, 70 mg of product polymer, M_w/M_n = 8600/7100 was obtained. ^{1}H NMR indicates that less than 10% of the I units of poly-I had been converted into I-Cl$_2$C=C=O units.

Reaction of Poly-I with Triethylamine. In a 100-mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar were placed diethyl ether (40 mL), poly-I (M_w/M_n = 278 000/117 000, 63 mg, 0.36 mmol), and triethylamine (0.25 mL, 1.81 mmol). The mixture was stirred at room temperature. After 5 h a 3-mL aliquot was removed. The ether was removed by evaporation under reduced pressure and the polymer obtained was dissolved in 1 mL of THF. Its molecular weight was analyzed by GPC, M_w/M_n = 232 000/112 000. A similar analysis after 17 h showed that the polymer molecular weight had further decreased, M_w/M_n = 199 000/84 000.

Reaction of Poly-I with Triethylamine Hydrochloride. The reaction of poly-I (M_w/M_n = 278 000/117 000, 63 mg, 0.36 mmol) and triethylamine hydrochloride (249 mg, 1.81 mmol) in diethyl ether (40 mL) was carried out as above. GPC analysis of the polymer after 5 h showed that its molecular weight had decreased to M_w/M_n = 228 000/112 600, while after 17 h its molecular weight distribution was found to be M_w/M_n = 188 600/57 300.

***cis*-1,4-Bis(trimethylsilyl)-2-butene.** *cis*-1,4-Bis(trimethylsilyl)-2-butene was prepared by literature methods.[27] ^{13}C NMR δ −1.68, 17.86, 123.15; ^{29}Si NMR δ 1.17.

2,2-Dichloro-*cis*-3,4-bis[(trimethylsilyl)methyl]cyclobutanone was prepared by the reaction of II with *cis*-1,4-bis(trimethylsilyl)-2-butene.[26] ^{1}H NMR δ 0.04 (s, 9 H), 0.09 (s, 9 H), 0.69 (t, 1 H, J = 14.4 Hz), 0.70 (t, 1 H, J = 14.4 Hz), 0.89 (dd, 1 H, J = 14.9 and 11.4 Hz), 0.91 (dd, 1 H, J = 14.9 and 9.7 Hz), 3.04 (td, 1 H, J = 10.2 and 5.3 Hz), 3.61 (td, 1 H, J = 11.1 and 5.3 Hz); for ^{13}C NMR, see Results and Discussion; ^{29}Si NMR δ 1.51, 2.06; IR ν 2955, 2898, 1804 (s), 1251 (s), 1192, 938, 862 (s), 781, 758 (m), 700 cm^{-1}.

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