Partial and complete chemical modification of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) by addition of dichloroketene

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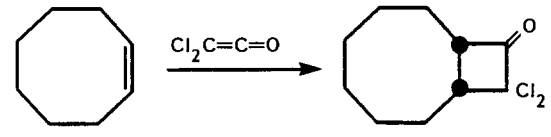
Dichloroketene, generated by the ultrasound-promoted dechlorination of trichloroacetyl chloride with zinc, has been added to the carbon–carbon double bonds of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (poly-I). The molecular-weight distribution of the adduct polymer in which all of the carbon–carbon double bonds have reacted with dichloroketene, poly[2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone dimethylsilylene], 100% poly(I–Cl_2C=C=O), has been characterized by gel permeation chromatography. The microstructure of 100% poly(I–Cl_2C=C=O) has been elucidated by ^1H, ^{13}C and ^{29}Si nuclear magnetic resonance as well as by infra-red spectroscopy. Similarly, a series of random copolymers have been prepared in which only some of the carbon–carbon double bonds of poly-I have reacted with dichloroketene. These have been characterized as above. The glass transition temperatures (T_g) of these copolymers, as well as that of 100% poly(I–Cl_2C=C=O), have been determined by differential scanning calorimetry. The T_g values are found to increase linearly with the percentage of the carbon–carbon double bonds of poly-I that have reacted with dichloroketene..

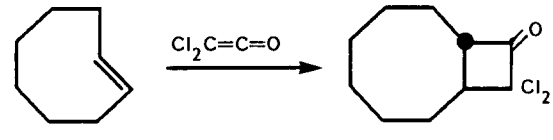
(Keywords: dichloroketene; addition; T_g values; copolymers)

INTRODUCTION

Dichloroketene (II) is well known to undergo cycloaddition reactions with the C–C double bonds of alkenes[1]. These [2 + 2] cycloaddition reactions proceed stereospecifically via a concerted [$\pi_s^2 + \pi_a^2$] reaction in which the π-system of the alkene and the C–C double bond of the ketene approach each other via an orthogonal trajectory[2]. These reactions yield 2,2-dichloro-3,4-disubstituted cyclobutanones in which the geometrical relationship of the substituents is identical to that in the starting alkene, i.e. *cis*-alkenes yield *cis*-cyclobutanones and *trans*-alkenes yield *trans*-cyclobutanones.



Cis-cyclooctene



Trans-cyclooctene

Unlike less reactive ketenes, II reacts even at room temperature with the C–C double bonds of unactivated alkenes, such as cyclopentene and cyclohexene[3]. Even with 1,3-dienes, which might react with II via a [2 + 4] pathway, [2 + 2] cycloaddition products (2,2-dichloro-3-vinylcyclobutanones) are obtained[4–6]. For example, [2 + 2] cycloaddition reaction of II with one of the C–C double bonds of 5-trimethylsilylcyclopentadiene yields 7,7-dichloro-4-*exo*-trimethylsilylbicyclo[3.2.0]hept-2-en-6-one[7,8]. Despite considerable interest in the reactions of allylic silanes[9], this is the only case of such a reaction.

The facile generation of II under mild experimental conditions from inexpensive readily available starting materials recommends this reaction. II can be generated either by the homogeneous dehydrohalogenation of dichloroacetyl chloride with triethylamine or by the heterogeneous dechlorination of trichloroacetyl chloride with active zinc[10]. The recent observation that ultrasound promotes this heterogeneous reaction further facilitates the preparation of 2,2-dichlorocyclobutanones[11].

2,2-Dichlorocyclobutanones are themselves versatile synthetic intermediates. For example, they can easily be converted to cyclobutanones by the dissolving metal reduction of the C–Cl bonds[12]. This transformation can also be achieved by reaction with tri-n-butyltin hydride[12]. They can likewise be modified under basic conditions to yield α-alkoxycyclopropane carboxylic acids via a Favorskii-type ring contraction reaction[13–15].

Despite the high reactivity of II discussed above, no examples of its reactions with C–C double bonds of unsaturated polymers such as *cis*-1,4-polybutadiene have been reported. This is surprising since there is considerable interest in the chemical modification of polymers[16–19]. Modification of functional groups in a polymer is one of the general routes for the synthesis of new polymeric materials. Many such reactions lead

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to polymers of reduced reactivity. For example, hydrogenation of the C–C double bonds of various unsaturated polymers leads to saturated polymers[20,21]. On the other hand, the addition of II to the C–C double bonds of an unsaturated polymer should yield an adduct polymer that has the potential for significant further chemical alteration.

EXPERIMENTAL

Characterization

^{1}H and ^{13}C n.m.r. spectra were obtained on a Bruker AM-360 spectrometer, while ^{29}Si n.m.r. spectra were run on an IBM Bruker WP-270-SY spectrometer. These were obtained operating in the Fourier-transform (*FT*) mode. Five per cent (w/v) solutions of polymer in chloroform-*d* were utilized to obtain ^{1}H n.m.r. spectra. Twenty per cent (w/v) solutions were used to acquire ^{13}C and ^{29}Si n.m.r. spectra. ^{13}C n.m.r. spectra were run with broad-band proton decoupling. Chloroform was used as an internal standard for ^{1}H and ^{13}C n.m.r. spectra. A DEPT[22] or NONOE[23] pulse sequence* was used to obtain ^{29}Si n.m.r. spectra. These were externally referenced to tetramethylsilane (TMS). *FT*i.r. spectra of films on NaCl plates were obtained on an IBM FT IR/30S, DTGS/CSI spectrometer.

Gel permeation chromatographic (g.p.c.) analyses of the molecular-weight distributions of the polymers were performed on a Waters system, comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 differential refractive index detector and a model 820 Maxima control system. A Waters 7.8 mm × 30 cm, 10 μm particle size, mixed pore size, crosslinked polystyrene gel column was used for the separation. The elution solvent was h.p.l.c.-grade tetrahydrofuran (THF) at a flow rate of 0.6 ml min^{-1}. The retention times were calibrated against known monodisperse polystyrene standards: M_p = 612 000, 212 400, 110 000, 20 400, 4800 and 1350 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis (t.g.a.) was carried out on a Perkin–Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3 min^{-1}. The temperature programme for the analysis was 50°C for 10 min followed by an increase of 4°C min^{-1} to 750°C. Glass transition temperatures of the polymers were measured on a Perkin–Elmer DSC-7 differential scanning calorimeter. The melting points of indium (m.p. 156°C) and spectro-grade hexane (m.p. −95°C) were used to calibrate the d.s.c. After equilibration at −100°C for 20 min, scans were conducted by increasing the temperature to 100°C at a heating rate of 20°C min^{-1}.

Chemical ionization high-resolution mass spectra (CIHRMS) with ammonia as the reagent gas were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determind by peak matching against known masses of perfluorokerosene.

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

Materials

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

*Distortionless enhancement by polarization transfer and nuclear Overhauser effect

*Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (poly-I)*

Poly-I (M_w/M_n = 541 000/353 000) was prepared by the anionic ring-opening polymerization of 1,1-dimethyl-1-silacyclopent-3-ene[24] cocatalysed by n-butyllithium and hexamethyl phosphoramide (HMPA) in THF at −78°C. Its properties were in agreement with literature values[25,26].

Cis-*1,4-bis(trimethylsilyl)-2-butene*

Cis-1,4-bis(trimethylsilyl)-2-butene (b.p. 67°C/3.0 mm Hg) was prepared in 22% yield by the dissolving metal reduction of 1,3-butadiene by sodium in THF in the presence of trimethylchlorosilane. ^{1}H n.m.r. and i.r. spectral data were in agreement with literature values[27]. ^{13}C n.m.r., δ = −1.68, 17.86, 123.15 ppm. ^{29}Si n.m.r., δ = 1.17 ppm.

*Synthesis of 2,2-dichloro-*cis*-3,4-bis(trimethylsilylmethylene)cyclobutanone (III)*

Cis-1,4-bis(trimethylsilyl)-2-butene (1.00 g, 5.02 mmol), zinc powder (1.64 g, 25.1 mmol) and 40 ml of diethyl ether were placed in a 100 ml three-necked round-bottomed flask equipped with a reflux condenser, a pressure equalizing addition funnel and a 0.5 inch ultrasonic probe, which was sealed with a rubber septum. The probe was connected to a Tekmar 500 W, 20 kHz high-intensity ultrasonic generator. The reaction flask was immersed in a room-temperature water bath to moderate the reaction temperature. Trichloroacetyl chloride (1.67 ml, 165.1 mmol) dissolved in 15 ml of diethyl ether was placed in the addition funnel. Zinc powder was subjected to activation by ultrasound (40% duty cycle at 20% energy output) for 10 min prior to addition of trichloroacetyl chloride. The reaction was conducted by the addition of trichloroacetyl chloride to the ultrasound-activated reaction mixture over 30 min. The reaction mixture becomes clear. Sonication was continued for an additional 10 min. The ethereal solution was decanted from the excess zinc and zinc chloride salts, which were washed with an additional aliquot of ether. The combined ether solution was washed with water and aqueous sodium bicarbonate until it was neutral. The organic layer was separated, dried over anhydrous magnesium sulphate, filtered and the ether removed by evaporation under reduced pressure. III was purified by fractional distillation (b.p. 98°C/0.3 mm Hg). A 92% yield, 1.43 g, was obtained. ^{1}H n.m.r., δ (ppm) = 0.04 (s, 9H), 0.09 (s, 9H), 0.67 (dd, 1H, J = 14.4 and 5.3 Hz), 0.71 (dd, 1H, J = 14.4 and 5.0 Hz), 0.89 (dd, 1H, J = 14.9 and 6.8 Hz), 0.92 (dd, 1H, J = 14.9 and 5.4 Hz), 3.04 (dt, 1H, J = 10.2 and 5.3 Hz), 3.61 (dt, 1H, J = 11.1 and 5.3 Hz). ^{13}C n.m.r., δ (ppm) = −1.31, −0.91, 13.19, 13.29, 47.55, 55.67, 89.17, 198.08. ^{29}Si n.m.r., δ (ppm) = 1.51, 2.06. I.r., ν (cm^{-1}) = 2955, 2898, 1804 (s), 1251 (s), 1192, 938, 862 (s), 781, 758, 700. CIHRMS $(M+18)^+$ *m/e* calculated for $C_{12}H_{28}Cl_2Si_2ON$, 328.1098; found; 328.1087.

Addition of dichloroketene to poly-I

Zinc powder (*Table 1*) and 60 ml of ether were placed in a reaction flask equipped as above. Ultrasound (10 min) was utilized to activate the zinc. At this point, poly-I (M_w/M_n = 541 000/353 000, 100 mg, 0.89 mmol) was added to the flask. A solution of trichloroacetyl chloride (*Table 1*) dissolved in 15 ml of ether was added to the ultrasound-activated reaction mixture over 25 min. The reaction mixture was subjected to ultrasound for 10 min after completion of the addition. The reaction was worked up as above. The dichloroketene adduct polymer was dissolved in a minimum amount of THF and was purified by precipitation from ethanol. This process was repeated. The purified polymer was dried under vacuum for 24 h at room temperature. Yields between 60 and 80% (*Table 1*) were obtained. Properties of 100% poly(I–Cl_2C=C=O) are as follows. ^{1}H n.m.r., δ (ppm) = 0.12–0.23 (br m, 6H), 0.75–0.90 (br m 2H), 0.95–1.06 (br m, 2H), 3.05–3.15 (br s, 1H), 3.60–3.70 (br s 1H). I.r., ν (cm^{-1}) = 2954, 2897, 1801 (s), 1253 (s), 1214, 1194, 1145, 1115, 1063, 938, 912, 851 (s), 734, 708. Elemental analysis calculated for $C_{18}H_{12}SiCl_2O$, C 43.06, H 5.42; found, C 43.32, H 5.84.

RESULTS AND DISCUSSION

We should like to report the addition of II to the C–C double bonds of poly-I to yield random adduct copolymers made up of 1,1-dimethyl-1-sila-*cis*-pent-3-ene and 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone dimethylsilylene units (*Figure 1*). We can economically express the percentage composition of such copolymers in terms of the percentage of the C–C double bonds of poly-I that have reacted with II. For example, the polymer in which all the C–C double bonds of poly-I have reacted with II will be called 100% poly(I–Cl_2C=C=O).

The II utilized in this reaction was generated under heterogeneous conditions by dechlorination of trichloroacetyl chloride in diethyl ether by zinc powder that was continuously activated by ultrasound. We have previously shown that, while there are significant problems, these are the optimal conditions. Among these problems ultrasound is known to degrade the molecular weight of high polymers. Further, the dechlorination of trichloroacetyl chloride by zinc yields not only II but also zinc chloride, which may combine with hydrochloric acid, formed by hydrolysis of trichloroacetyl chloride with adventitious water, to yield the strong acid $H^+(ZnCl_3)^-$. Allylic silanes undergo cleavage of the allylic Si–C bond on treatment with protic acids[9]. In control experiments, we have shown that poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene), a closely related polymer, is degraded by ultrasound as well as by zinc chloride in the absence of ultrasound. Addition of pyridine failed to eliminate this problem. Finally, attempts to utilize the homogeneous dehydrohalogenation reaction of dichloroacetyl chloride with triethylamine to generate dichloroketene failed to give either reasonable yields or high conversion to poly(I–Cl_2C=C=O)[28].

For these reasons, we have utilized the heterogeneous reaction of trichloroacetyl chloride and zinc activated by ultrasound to generate II. We have chosen the experimental parameters to achieve the highest molecular weight of poly(I–Cl_2C=C=O). The reaction time has been minimized to diminish the cleavage of polymer by ultrasound. Zinc powder was activated by treatment with ultrasound prior to addition of poly-I to the reaction. Nevertheless, to achieve reaction of a high percentage of the C–C double bonds of poly-I requires the generation of a large excess of II. These conditions expose the remaining allylic Si–C linkages in the partially modified copolymer to large excess of zinc chloride. The result is that, as the extent of chemical modification increases, the molecular weight and yield of the copolymer decrease. The decrease in the yield probably results from the copolymer purification process in which low-molecular-weight oligomers are not precipitated by methanol from THF.

The thermal stability of 100% poly(I–Cl_2C=C=O) in a nitrogen atmosphere has been determined by t.g.a. It is less thermally stable than poly-I (*Figure 2*). The 100% poly(I–Cl_2C=C=O) is stable to 140°C. Between 140 and 205°C, 10% of the initial sample weight is lost. Rapid weight loss (38%) occurs between 205 and 225°C. Slow weight loss (4%) occurs between 255 and 285°C. Between 285 and 465°C, 14% weight is lost. Finally, between 465 and 525°C, 3% weight is lost. A dark blue residue amounting to 30% is stable to at least 750°C.

The glass transition temperatures (T_g) of these copolymers have been determined by d.s.c. The T_g values of dichloroketene adduct polymers whose composition is intermediate between poly-I and 100% poly (I–Cl_2C=C=O) increase linearly with the percentage of chemical modification (*Figure 3*). This is somewhat surprising since the properties of low-molecular-weight

Table 1 Effect of molar ratio of trichloroacetyl chloride and zinc with respect to poly-I on the percentage composition, M_w/M_n, yield and T_g of the dichloroketene adduct copolymers

Ratio Cl_3CCOCl	Ratio Zn	Per cent composition[a]	$(M_w/M_n)\times10^{-3}$	Yield (%)	T_g (°C)
0	0	0	541/353		−63
1	2	16	283/161	79	−51
3	5	42	195/113	74	−24
6	10	64	32/18	68	−21
8	15	82	18/11	65	−12
8	20	100	22/15	61	8

[a] Per cent composition = $n'/(n'+m')$ (see *Figure 1*)

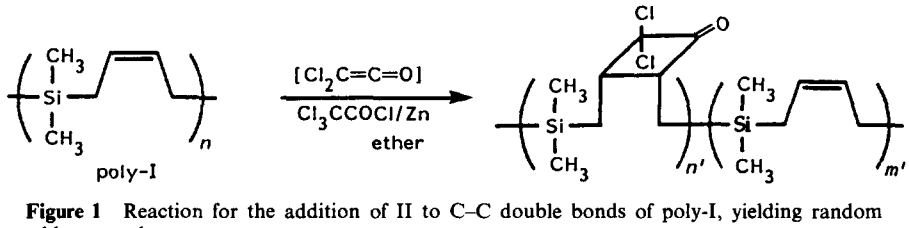


Figure 1 Reaction for the addition of II to C–C double bonds of poly-I, yielding random adduct copolymer

polymers often change with increasing molecular weight[29]. Apparently, the molecular weights of these copolymers are sufficiently high that their T_g values are not affected by differences in their molecular weights but only by the extent of their chemical modification. Such linear relationships of properties and percentage composition of copolymers have been frequently observed[30,31].

High-field n.m.r. spectroscopy permits us to analyse partially the complex microstructure of 100% poly(I–$Cl_2C{=}C{=}O$). The ^1H n.m.r. spectrum of 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone units (*Figure 4*) has been assigned by comparison with the ^1H n.m.r. spectra of III (*Figure 5*).

Only single resonances are observed in the ^{13}C n.m.r. for the carbonyl carbon (197.88 ppm), the dichloro-substituted carbon (88.94 ppm) as well as the C3 (47.38 ppm) and C4 (55.65 ppm) methine carbons of the 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone units. On the other hand, seven resonances are observed for

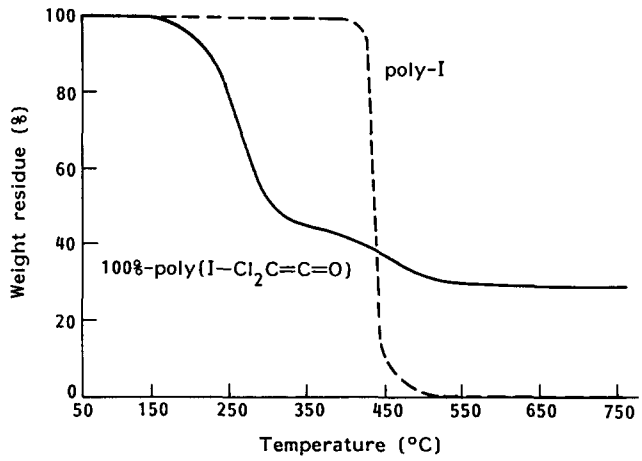


Figure 2 T.g.a. of poly-I and 100% poly(I–$Cl_2C{=}C{=}O$)

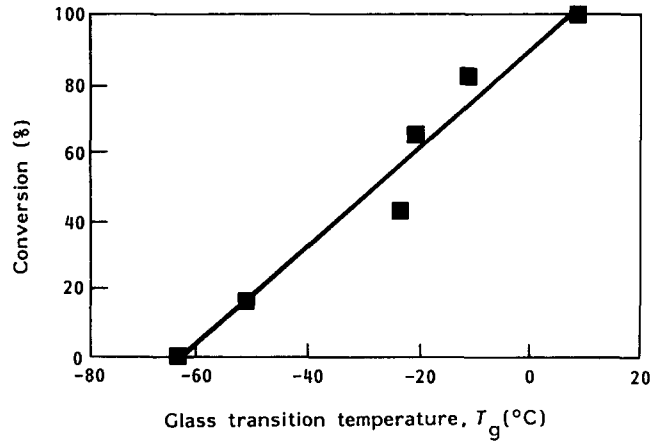


Figure 3 Plot of glass transition temperature T_g (°C) vs. percentage conversion of poly(I–$Cl_2C{=}C{=}O$)

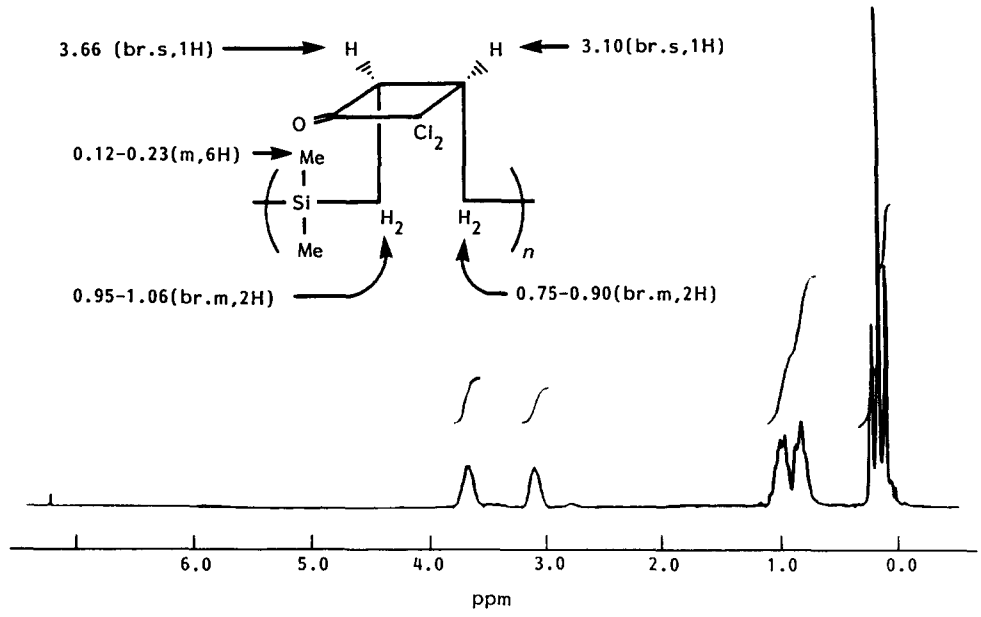


Figure 4 ^1H n.m.r. spectrum of 100% poly(I–$Cl_2C{=}C{=}O$)

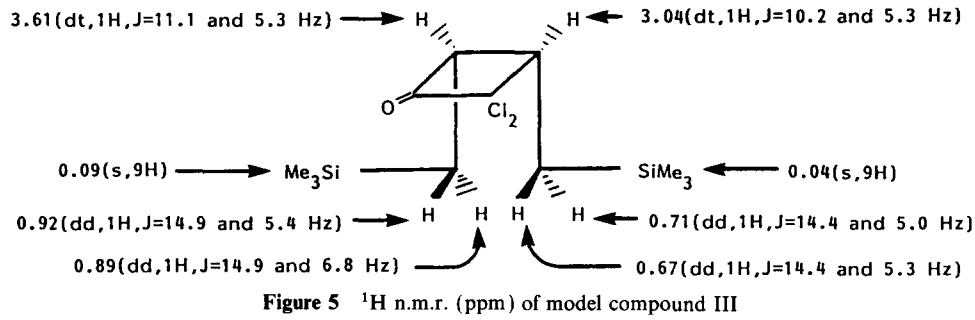


Figure 5 ^1H n.m.r. (ppm) of model compound III

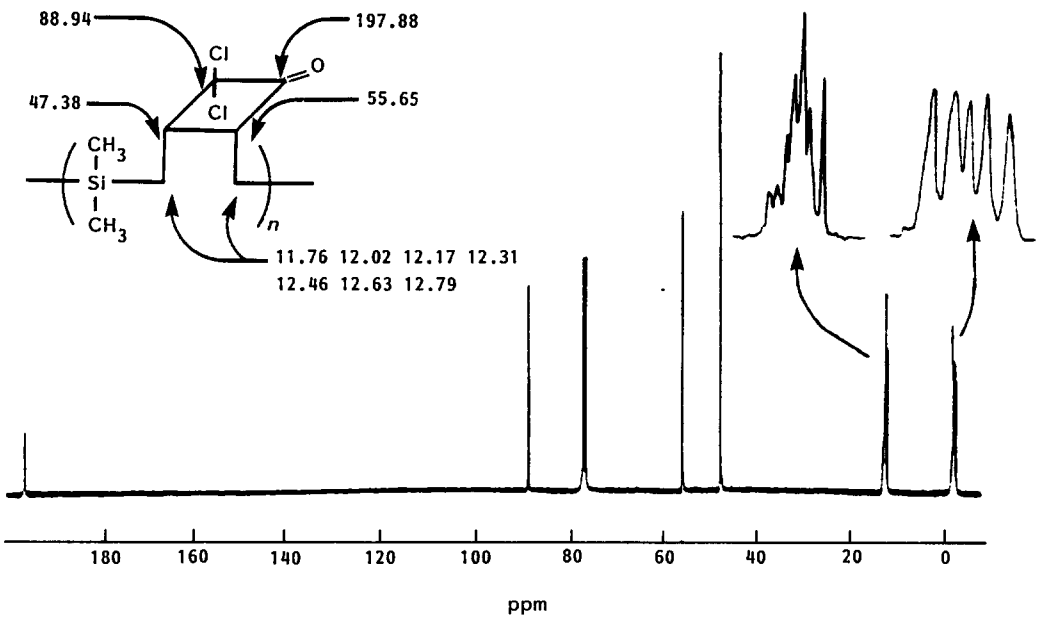


Figure 6 ^{1}H n.m.r. spectrum of 100% poly(I–Cl_2C=C=O)

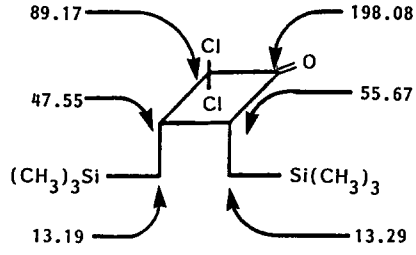


Figure 7 ^{13}C n.m.r. (ppm) of model compound III

the methylene carbons: δ = 11.76, 12.02, 12.17, 12.31, 12.46, 12.63, 12.79 ppm. This observation can be accounted for in terms of a triad analysis in which the methylene carbons are sensitive to both the orientation (head or tail) as well as the geometrical arrangement with respect to the polymer chain (*syn* or *anti*) of nearest-neighbour 2,2-dichlorocyclobutanone. Eight distinct methylene groups are predicted by this analysis. Apparently two of the lines fortuitously are coincident (*Figure 6*). These assignments have been confirmed by comparison with those observed for III (*Figure 7*).

A dyad analysis of the dimethylsilylene units of 100% poly(I–Cl_2C=C=O) predicts three pairs or six distinct microenvironments. Thus adjacent 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone units can be in head-to-head, head-to-tail or tail-to-tail (1:2:1) relationship to one another. Each of these microenvironments is split to a pair by the fact that adjacent 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone units can be on either the same side or opposite sides of the polymer chain (*syn* or *anti*) (*Figure 8*). In the ^{1}H n.m.r. three signals at 0.12, 0.18 and 0.23 ppm in a 1:2:1 ratio are observed for the methyl hydrogens (*Figure 4*). This is consistent with the dyad analysis if the differences due to head-to-head compared to head-to-tail or tail-to-tail are more important than the geometrical *syn* or *anti* relationship of adjacent 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone units in differentiating microenvironments. On the other hand, in the ^{13}C n.m.r. five distinct resonances are observed: δ = −1.78, −2.01, −2.18, −2.35 and −2.59 ppm. Apparently, two of the six microenvironments fortuitously lead to an overlap of ^{13}C n.m.r. signals. The ^{29}Si n.m.r. is similar to the ^{1}H n.m.r. in that only three resonances are observed: δ = 3.62, 3.12 and 2.55 ppm (1:2:1).

A series of copolymers have been prepared by addition of II to some of the C–C double bonds of poly-I. These random copolymers contain both 1,1-dimethyl-1-sila-*cis*-pent-3-ene and 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone units. The ratio of these in the copolymers can be easily determined from the ^{1}H n.m.r. spectra by comparison of the integral due to the methyl groups bonded to silicon, which are present in both of these, to the resonance at 5.29 ppm due to the vinyl hydrogens of the 1,1-dimethyl-1-sila-*cis*-pent-3-ene units.

The microstructures of these copolymers have been determined by ^{1}H, ^{13}C and ^{29}Si n.m.r. spectroscopy. The dimethylsilylene units in the copolymers can have 1,4-*cis*-2-butene and/or 2,2-dichloro-*cis*-3,4-bis(methylene) cyclobutanone units as nearest neighbours. A dyad analysis leads to a prediction of nine possible microenvironments. At very low extent of chemical modification, most of the dimethylsilylene units will have two 1,4-*cis*-2-butene units as nearest neighbours. These will have spectra almost identical to that of poly-I. At high levels of chemical modification, the spectra of the dimethylsilylene groups will be essentially that of dimethylsilylene units in 100% poly(I–Cl_2C=C=O), six microstructures, as discussed above. At intermediate conversion, some of the dimethylsilylene units will be in unsymmetrical environment in which a 1,4-*cis*-2-butene is on one side and a 2,2-dichloro-*cis*-3,4-bis(methylene) cyclobutanone is on the other. This leads to two equally probable microenvironments, since the dimethylsilylene unit can be either close to or distant from the carbonyl group of the 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone ring (*Figure 9*). The methyl groups of the dimethylsilylene units are in fact diastereotopic. This leads to a prediction of four distinct microenvironments for the methyl groups in such unsymmetrical situations. In the ^{1}H n.m.r. only two signals are observed for the

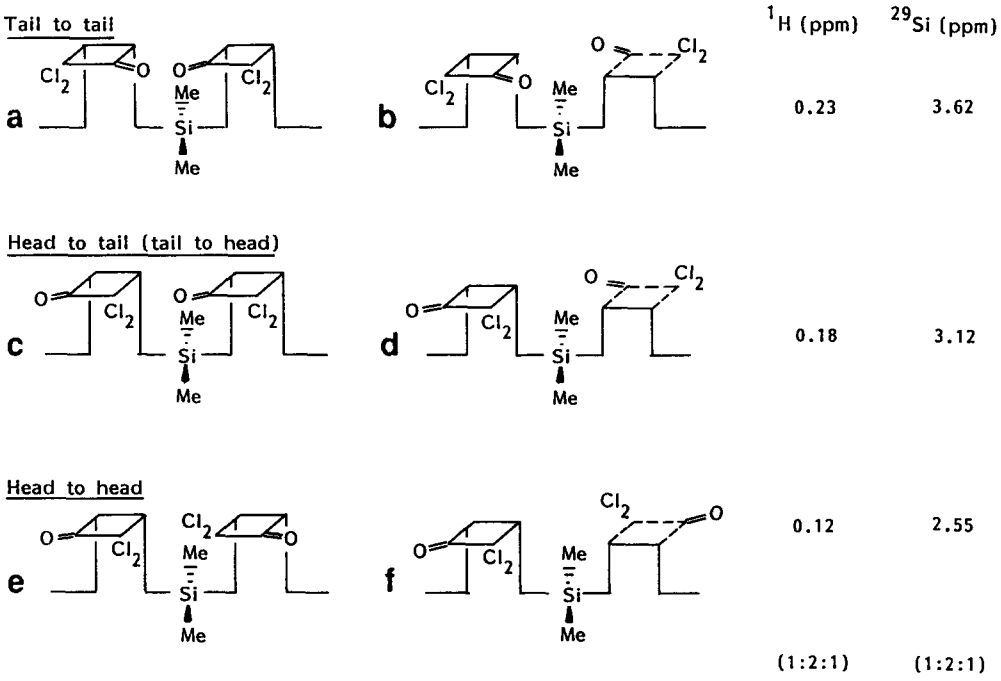


Figure 8 Dyad microstructures of 100% poly(I–Cl_2C=C=O)

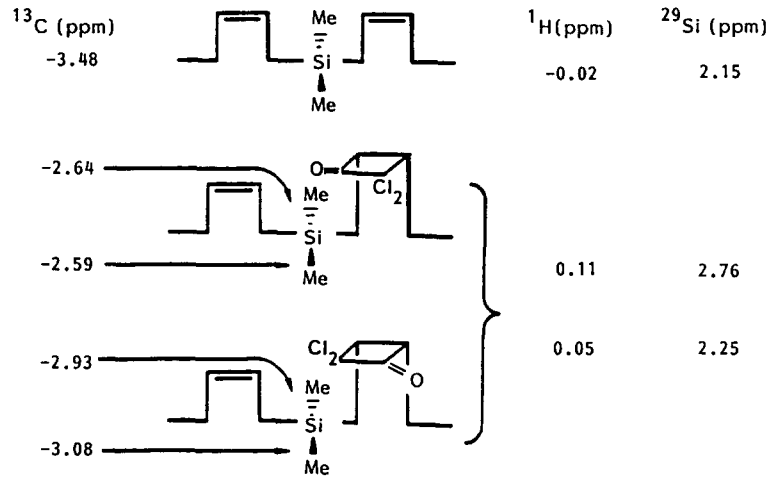


Figure 9 Dyad microstructure of low and intermediate conversion of poly(I–Cl_2C=C=O)

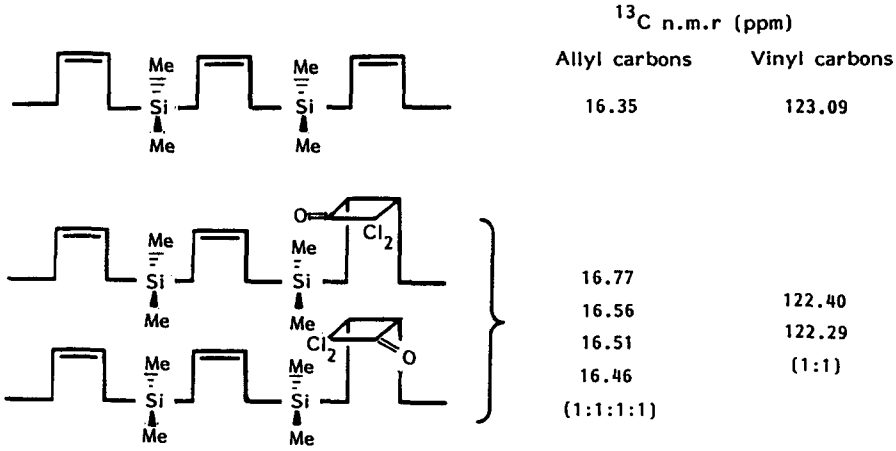
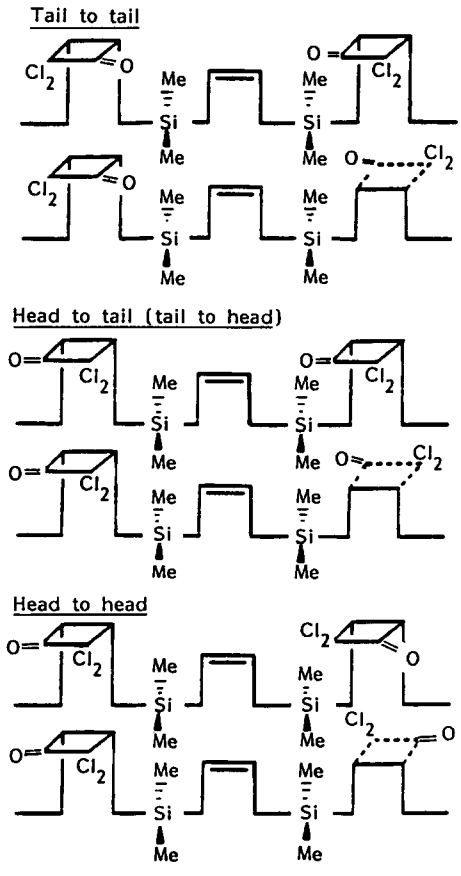


Figure 10 Triad microstructures of low and intermediate conversion of poly(I–Cl_2C=C=O)



^{13}C n.m.r (ppm)

Allyl carbons	Vinyl carbons
16.96	123.96
16.90	123.87
16.63	123.74
16.57	(1:2:1)
(3:1:3:1)	

Figure 11 Triad microstructures of high conversion of poly(I–Cl_2C=C=O)

methyl hydrogens at 0.11 and 0.05 ppm (1:1). Apparently, there is not sufficient dispersion in the ^{1}H n.m.r. at 360 MHz to detect the diastereotopic differences. On the other hand, in the ^{13}C n.m.r. a total of four signals, consistent with the dyad analysis, are observed: $\delta = -2.59$, -2.64, -2.93 and -3.08 ppm. The ^{29}Si n.m.r. spectrum is similar to ^{1}H n.m.r. in that only two signals are observed at 2.76 and 2.25 ppm in a 1:1 ratio.

A triad analysis of the 1,4-*cis*-2-butene units in such copolymers predicts a total of nine microstructures (*Figures 10* and *11*). At low conversion, a symmetrical microstructure with 1,4-*cis*-2-butene on either side similar to that of poly-I occurs. In the ^{13}C n.m.r. spectrum, single resonances at 16.35 and 123.09 ppm are observed. These are assigned respectively to the allyl and vinyl carbons. At intermediate conversion, two unsymmetrical microstructures are found. In these a 1,4-*cis*-2-butene unit is found on one side while a 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone is on the other. Consistent with this analysis, four ^{13}C n.m.r. signals due to allyl carbons in such unsymmetrical environments are observed: $\delta = 16.46, 16.51, 16.56$ and 16.77 ppm (1:1:1:1). On the other hand, only two signals are observed for the vinyl carbons: $\delta = 122.40$ and 122.29 ppm (*Figure 10*).

Finally at high conversion, the 1,4-*cis*-2-butene units are found in six environments in which 2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone rings are neighbours on both sides (*Figure 11*). This triad analysis predicts a total of eight distinct allylic microenvironments. In fact, only four lines are observed in the ^{13}C n.m.r. spectrum: $\delta = 16.96$, 16.90, 16.63 and 16.57 ppm (3:1:3:1). Likewise, only three signals are detected for the vinyl carbons: $\delta = 123.96$, 123.87 and 123.74 ppm (1:2:1). Apparently, a number of these resonances fortuitously overlap. There is excellent agreement between the prediction of both the dyad and triad analysis and the observed spectra.

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