Returning to eq 8, we now write $g(\nu, t)$ as a Taylor series about ν_0, and get

$$\theta = \frac{T_0}{2\pi}\int_{-\infty}^{+\infty} \exp\left\{g(\nu_0, t) + \frac{g''(\nu_0)}{2!}(\nu - \nu_0)^2 + \ldots\right\}\mathrm{d}\nu \quad (13)$$

The term $g''(\nu_0)$ is the second derivative of $g(\nu_0, t)$ with respect to ν evaluated at ν_0, and it is not a function of t. Neither, of course, are any of the higher derivatives. It has been shown[5] that for sufficiently large values of t only the first two terms in the series are required, and we obtain

$$\theta = \frac{T_0}{2\pi(KG^* + k^*)}\exp(i\nu_0 t)\int_{-\infty}^{+\infty} \exp\left\{\frac{1}{2}g''(\nu_0)(\nu - \nu_0)^2\right\}\mathrm{d}\nu \quad (14)$$

Since it can be shown that the real part of $g''(\nu_0)$ is negative, the above integral exists. The product of the integral and the factor in any system is a constant, so we can write

$$\theta = \theta_0 \exp(i\nu_0 t) \quad (15)$$

Or by identifying ν_0 with the decay frequency of the pendulum after steady damped sinusoidal motion has been established, we can write

$$\theta = \theta_0 \exp(i\omega t) \quad (16)$$

Now if we express ω in its complex form

$$\omega \equiv \nu_0 \quad (17)$$

where

$$\omega = \omega' + i\omega'' \quad (18)$$

the final result is

$$\theta = \theta_0 \exp(i\omega' t - \omega'' t) \quad (19)$$

We thus find that the limiting behavior of a torsion pendulum (in this case coupled to a dynamic viscometer) after being given an impulsive loading is as a damped harmonic oscillator, and we can use the frequency (ω') and damping constant (ω'') to determine G^* without assuming any rheological model.

From eq 12, 17, and 19 we find that if $G^* = G' + iG''$ and $k^* = k' + ik''$

$$G' = [I(\omega'^2 - \omega''^2) - k']/K \quad (20)$$

$$G'' = (I2\omega'\omega'' - k'')/K \quad (21)$$

The complex constant k^* can be determined from the dynamic behavior of the system without polymer solution in the viscometer. The geometric constant K can be determined for any cup-and-bob or cone-and-plate combination by calibration with a nonviscoelastic Newtonian fluid.

By changing the interpretation of the various constants, one could apply the above analysis to any freely damped linear viscoelastic system.

One subtle aspect of the results is that G^* is determined at a complex value of the angular frequency. But, as was pointed out by Struik,[2] the loss modulus can be determined at real frequencies by analytic continuation using a Taylor series. We wish to point out, however, that in many cases (and indeed maybe most cases) of interest to polymer rheologists, the correction to real frequencies is a small one. Measurements with freely damped systems are most easily made when $\omega' \gg \omega''$. If this inequality holds, the Cauchy–Riemann equations[6] give

$$G'(\omega') = G'(\omega' + i\omega'') + \frac{\partial G''}{\partial \omega'}\,\omega'' \quad (22)$$

$$G''(\omega') = G''(\omega' + i\omega'') - \frac{\partial G'}{\partial \omega'}\,\omega'' \quad (23)$$

to the first order in ω'', where the derivatives are evaluated at the real frequency ω' ($\omega'' = 0$). If we write the above equations in terms of the errors in G' and G'' we find

$$\frac{G'(\omega') - G'(\omega' + i\omega'')}{G'(\omega')} = \tan\delta\,\frac{\partial \ln G''}{\partial \ln \omega'}\left(\frac{\omega''}{\omega'}\right) \quad (24)$$

and

$$\frac{G''(\omega') - G''(\omega' + i\omega'')}{G''(\omega'')} = -\frac{1}{G''}\,\frac{\partial G'}{\partial \ln \omega'}\left(\frac{\omega''}{\omega'}\right) \quad (25)$$

where $\tan\delta = (G''/G')$. For all polymer systems the absolute value of $(\partial \ln G''/\partial \ln \omega)$ is less than or equal to 1.0; in addition, $\tan\delta$ rarely exceeds 1.0. Furthermore, approximate relationships between viscoelastic functions[1] can be used to show that $G'' \sim (\partial G'/\partial \ln \omega)$. It follows, therefore, that the correction to G' and G'' can be made as small as desired by making (ω''/ω') sufficiently small, for example as in the previously mentioned work with concentrated polystyrene solutions.[3]

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Notes

Production of Organometallic Polymers by the Interfacial Technique. XVI. Importance of Hydrolysis in the Synthesis of Poly[oxyadipoyloxy(diphenylsilylene)][1]

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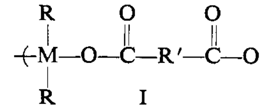
Recently we have been interested in the synthesis of group IV polyesters of the below form using the interfacial technique.[2,3]



$$\left(\!\!-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{M}}}}-O-\overset{\displaystyle O}{\overset{\|}{C}}-R'-\overset{\displaystyle O}{\overset{\|}{C}}-O-\!\!\right)$$

I

Hydrolysis is important in the aqueous interfacial reaction between organodichlorosilanes or organodichlorostannanes

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(1) This study was supported by an American Chemical Society Petroleum Research Fund Grant No. 1338 G 13.

(2) (a) C. Carraher and R. Dammeier, *Makromol. Chem.*, **135**, 107 (1970); (b) C. Carraher and R. Dammeier, *J. Polym. Sci., Part A-1*, **8**, 3367 (1970).

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TABLE I
POLYMER PHYSICAL PROPERTIES AS A FUNCTION OF VOLUME OF AQUEOUS PHASE[a]

Volume of water added	% yield	LVN, ml/g[b]	Softening range, °C	Ratio of siloxane to carboxyl units[c]
3	21	12.4	227–240	1.0
10		10.4	76–82	1.6
20	29	6.8	68–72	1.9
50	36	5.2	62–66	2.0
100	44	3.6	40–44	2.9

[a] Reaction conditions: 0.005 mol of diphenyldichlorosilane in 50 ml of benzene; 0.005 mol of disodium adipate in various volumes of water; run for 0.50 min at 30° at a stirring speed of 17,000 rpm. [b] Viscosities run in dimethyl sulfoxide. [c] Calculated from comparison of infrared spectra of products—specifically the Si-phenyl and carbonyl bands at 1440 and 1735 cm^{-1}, respectively.

with diols or diamines.[4–7] In the case of organodichlorosilanes hydrolysis is sufficiently important to prevent inclusion of the diol or diamine moiety. The carboxylate ion is more nucleophilic (with a Swain–Scott nucleophilic constant of 2.7[8]) than either a diol or diamine and competes favorably with water to form small linear products of form I when the aqueous phase consisted of a saturated solution of the dicarboxylate ion (generally in the range of a 3 *M* solution of the carboxylate ion). Optimum concentrations of reactants for interfacial polymerizations are generally in the range of 0.1–0.01 *M*.[9]

In the interfacial reaction of dibutyltin dichloride with sodium adipate hydrolysis was found to occur (to produce Sn–OH end groups), but polymerization rate and polymer molecular weight were constant as the volume of water (amount of reactants held constant) was increased 30-fold. In addition the products contained no infrared detectable amounts of Sn–O–Sn bonding.[2b]

The general order of hydrolysis for group IV organometallic chlorides is Si > Sn.[10] It is the purpose of this paper to report the relative importance of hydrolysis of organosilicon chlorides (in particular diphenyldichlorosilane) in the interfacial synthesis of polyesters of form II.

The reaction procedure is described in detail elsewhere.[2] In general organometallic dichlorides in an organic solvent are added to stirred solutions of diacid salts in water. Softening ranges were determined on a Fisher–Johns melting point apparatus at an approximate heating rate of 2°/min. Viscosity was determined in dimethyl sulfoxide at 30° using a Cannon–Ubbelohde viscometer. Limiting viscosity numbers (LVN, ml/g) were obtained by serial dilution of solutions of 1 g/100 ml and less.

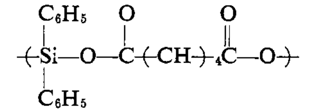
Table I presents yield, molecular weight, and softening range results as a function of volume of the aqueous phase. Product LVN decreases as the volume of water increases, but yield increases. The aqueous volume varied approximately 30-fold (representing an approximate range of 0.03–0.0009 mol of adipate compared to 1 mol of water).

Other physical properties varied. As the volume of water increased the products changed in color and texture from white and flaky to light tan and glassy at high volumes of water. The solubility properties of the products also varied. For instance, the products produced at low volumes of water were insoluble in acetone while the products produced at high water volumes were soluble in acetone. This may be due to a difference in product composition and/or molecular weight since the products produced at high volumes of water are lower molecular weight and thus may possess a wider solubility range.

Infrared spectra were obtained employing a Beckman I.R. 12 or Perkin–Elmer 237 instrument using potassium bromide pellets for solids and employing the procedure described by Carraher[11] for liquids. Assignments were made by comparing spectra of parent and similar compounds, poly[oxy(diphenylsilylene)] and other group IV products, and using band assignments given previously in literature.

Pertinent infrared assignments are as follows for poly[oxyadipoyloxy(diphenylsilylene)] and poly[oxy(diphenylsilylene)]: SiOC=O– 1190 and 922 cm^{-1} (lit.[12,13] 1190–1135 and 980–920), Si–Cl 560 cm^{-1} (lit.[12,14–16] 610–420), Si–OH 3200–3300 cm^{-1} (lit.[12,14] 3700–3200), C=O 1710–1720 cm^{-1} (lit.[12,17–19] 1700–1750), SiOSi (asymmetric) 1020–1030 cm^{-1} (lit.[12,14,16,18,20] 1000–1100).

Infrared and elemental analyses of the product produced at 3 ml of added water (representing a saturated adipate solution) were in agreement with a product having a repeating unit described below. The band around 560 cm^{-1} is missing in the spectra of all polyesters, indicating an absence of infrared-detectable SiCl end groups.



$$-\!\!\left(\overset{C_6H_5}{\underset{C_6H_5}{\mathrm{Si}}}-O-\overset{O}{C}-(CH)_4-\overset{O}{\overset{\|}{C}}-O\right)\!\!-$$

II

As the volume of water increases several distinctive spectral trends are evident. Bands attributed to the presence of the silicon portion increase in size relative to bands attributed to the carboxylate portion.[21] The SiOH band increases with increase in water volume. The increase in the SiOH band is a consequence of additional SiOH end groups which may result from a larger proportion of SiOH end groups and/or is a consequence of shorter chains offering more SiOH end groups per volume of product.

A band about 1025 cm^{-1} attributed to SiOSi stretching appears in the product of the system utilizing 20 ml of H_2O

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(21) Elemental analysis is not considered a strong indication of varying amounts of siloxane units included in the chain for the present system since the percentage differences between the polyester and siloxane units are small. Elemental analysis for systems using low volumes of water where siloxane and polyester elemental analysis differ significantly are in agreement with a polyester repeating unit. Carbon and hydrogen values are as follows: poly[oxy(diphenylsilylene)] dimer % C = 69, % H = 5.2; poly[oxyadipoyloxy(diphenylsilylene)] % C = 66, % H = 5.5; diphenyldihydroxysilane % C = 67, % H = 5.5; experimentally determined (PCR, Inc., Gainesville, Fla.) for product from the 50-ml water system listed in Table I % C = 65, % H = 5.4.

(Table I) and increases in size as the water volume increases. Thus the relative silane content in the products increases as the water volume increases. This increase presumably occurs *via* two routes—incorporation of silane as siloxane (SiOSi) units and as (a greater number of) SiOH end groups.

Siloxane units probably are the result of the following sequence of steps

$$\equiv\text{SiCl} \overset{\text{step 1}}{\xrightarrow[-\text{HCl}]{\text{H}_2\text{O}}} \equiv\text{SiOH} \overset{\text{step 2}}{\xrightarrow[-\text{HCl}]{\equiv\text{SiCl}}} \equiv\text{SiOSi}\equiv$$

Step 2 is believed to be slower than the desired reaction between SiCl and carboxylate ion. This is substantiated by the absence of detectable SiOSi units in reactions at low volumes of water even though the presence of SiOH is evidenced. In addition the interfacial synthesis of siloxanes from analogous systems produces chains generally about two to three units long compared with degrees of polymerization of 30 for the silicon polyester produced at low volumes of water. As is true with many interfacial systems the desired condensation step is probably in competition with other rapid steps and thus has a "tight reaction schedule" regarding polymer formation and growth. At higher volumes of water, hydrolysis is believed to become more important thus lowering the SiCl concentration. As water volume increases the reaction occurs to a greater degree *via* the slower step 2 than the desired pathway to polyester, possibly accounting for the decrease in molecular weight.

The yield trend is more difficult to explain. It is possible that a competing reaction for the silane is the formation of cyclic siloxanes. Such cyclic siloxanes are probably soluble in the organic phase (for instance 20) and thus are not collected as products. Linear siloxanes are insoluble in the reaction system and thus would be counted as yield. (The absence of detectable amounts of tetracyclic siloxanes is indicated by the absence of bands in the 1070–1090-cm^{-1} region.[18,20]) It is possible that the effect of increase in water volume enhances formation of linear siloxanes relative to (and at the expense of) cyclic siloxane formation, resulting in a greater yield of product at higher volumes of water. It is found for analogous systems under similar reaction conditions that yield of linear siloxane increases as aqueous volume increases. While the above may not be the answer, it offers a reasonable possibility. Differences in the ratio of adipate to water molecules and in diffusion rates of the adipate caused by changes in aqueous volume also may play a role in determining the product trend.

Hydrolysis is important in the interfacial synthesis of both the tin and silicon polyesters. It is not critical in tin polyester producing systems but is critical in silicon polyester synthesis. This is in keeping with the experimentally observed trend of group IV halide hydrolysis of Sn < Ge < Si.

Stereospecific and Asymmetric Inclusion Polymerization. II. The Effect of Pressure and Temperature on the Polymerization of *trans*-1,3-Pentadiene Included in Racemic Perhydrotriphenylene

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In a previous paper of this series,[2] we described two methods of polymerization of 1,3-pentadiene in the included state. The first consists of the irradiation of the monomer–perhydrotriphenylene (PHTP) inclusion compound, the second of the polymerization of the monomer in the presence of preirradiated pure PHTP. In the first case, by vapor pressure measurements, by differential thermal analysis, and by X-ray examination, we demonstrated that the starting material and the reaction product are the crystalline adducts of PHTP–pentadiene and PHTP–polypentadiene, respectively.

In the second case, we proposed a reaction scheme in which the inclusion of monomer into preirradiated PHTP precedes the polymerization. This scheme seems very likely since the polymerization rate is very low and the monomer was introduced into the reaction vial in the liquid state and in large excess.

In this paper we give decisive evidence supporting this scheme, which was obtained under more severe conditions, *i.e.*, by introducing the monomer in the gaseous state and in a controlled amount.

Experimental Section

Runs were carried out in small glass apparatus consisting of two vials separated by a break-seal (Figure 1). A weighed amount of monoclinic PHTP was placed in A and an excess of monomer was distilled in B. Both A and B were degassed and sealed under vacuum. PHTP was irradiated by a ^{60}Co source of 4000 Ci, with a dose rate of 0.6 Mrad/hr. If during irradiation the monomer was present in B, it was shielded by lead bricks; however, in most cases, the monomer was introduced into B after irradiation. The diaphragm was broken after placing A and B into thermostated baths ($t_A > t_B$); in this way, the temperature of the solid phase (t_A) and the monomer pressure ($p = f(t_B)$) were kept constant during the run. For absorption measurements, vessel B consisted of a calibrated tube having convenient dimensions to guarantee an accuracy of reading ±1% of the stoichiometric amount. The yield of polymerization was determined by weighing the polymer insoluble in boiling acetone, after complete extraction of PHTP. The preparation of PHTP and its characterization are reported in a previous paper.[3]

Results and Discussion

The rate of inclusion of gaseous *trans*-1,3-pentadiene in nonirradiated PHTP was measured at 30° and at pressures ranging between 141 and 460 Torr (t_B between 0 and 28°) (Figure 2). Below the decomposition pressure of the adduct (which at 30° equals 313 Torr), no absorption of pentadiene in PHTP takes place.

In the field of pressures between the decomposition pressure of the adduct and the vapor pressure of the saturated solution, the absorption of the guest component has a rate that depends on pressure and stops at an equilibrium value. Such a value coincides with that obtained by reaching equilibrium from the opposite side, *i.e.*, after distilling an excess of monomer from B to A.

From these experiments, we determined the stoichiometry of the adduct; it contains 76 mg of pentadiene/g of PHTP. To this value corresponds a repetition period of 8.7 Å per pentadiene molecule along the channel axis (for a comparison with other guest molecules, see other papers of ours[4,5]). When

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