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The Fundamental Basis for Cyclopolymerization. I. Unconjugated Chromophoric Interactions Related to Cyclopolymerization[†]

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SUMMARY

A far ultraviolet study showed progressive bathochromic wavelength shifts within the following series of compounds: (i) allyltrimethylsilane, diallyldimethylsilane, triallylmethylsilane, tetraallylsilane; (ii) allyltripropylsilane, diallyldipropylsilane, triallylpropylsilane; (iii) 4,4-dimethyl-1-pentene, 4,4-dimethyl-1, 6-heptadiene, 4-allyl-4-methyl-1,6-heptadiene. In the series trimethylvinylsilane, dimethyldivinylsilane, methyltrivinylsilane, and tetravinylsilane, trimethylvinylsilane was shifted bathochromically from the rest of the vinylsilanes, which were grouped together. Allyldimethylvinylsilane showed two independent absorptions.

A homoconjugative, interspatial interaction is postulated as the cause of the progressive bathochromic shifts observed. The structures depicting this interaction are found to coincide with the structures postulated for the transition state of intra-intermolecular cyclopolymerization. The activation energy ratios for the free radical polymerization of the allylmethylsilanes are also found proportional to the shift ratios from the ultraviolet study.

4,4-Dimethyl-1,6-heptadiene and 4-allyl-4-methyl-1,6-heptadiene were

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cyclopolymerized using a Ziegler catalyst. The physical properties of the soluble polymers obtained are reported.

INTRODUCTION

It has been suggested [1] that a homoconjugative interaction between ethylenic bonds may account for the unique tendency of unconjugated diene systems to cyclopolymerize. Such a phenomenon would have a stabilizing influence on the excited state of the molecule, thus providing an energetically favorable path from diene to cyclic product.

An extensive body of evidence [2-8] supports the interaction of nonconjugated chromophores. Evidence for the interaction is provided by the ultraviolet spectra, which differ from those of the insulated chromophores. The spectral effects are usually bathochromic shifts or the appearance of new peaks; they have been observed in unconjugated dienes capable of cyclopolymerization, such as trans-1,3,8-nonatriene [9], 1,3,6,8-nonatetraene, 1,3,9,11-dodecatetraene [10, 11], and dimethylenecyclohexane [12, 13]. The spectroscopic data obtained by van Heinigen [12] for the methylenecyclohexanes are reported in Table 1. The authors postulated that the

Table 1. Ultraviolet Absorption of Methylenecyclohexanes [12]

	95% Ethanol		Isooctane	
Compound	λ_{max}, mμ	E	λ_{max}, mμ	E
Methylenecyclohexane	191.8	10,850	191.3	11,700
			197.5	9,200
1,4-Dimethylenecyclohexane	198.6	19,500	198.2	21,100
	202.3	17,200	202.8	18,500
	208.9	9,550	208.6	10,300

(I) (II)

interactions observed in the ultraviolet spectra also represent the transition states in the cyclic intra-intermolecular polymerizations. For 1,3,6,8-nonatetraene, for example, structures **(I-II)** were drawn.

The examples reported, however, are isolated, and the conclusions reached are sometimes uncertain. It was thought that more conclusive evidence could be obtained by investigating series of compounds exhibiting an increasing number of unconjugated double bonds. The first series considered was mono-, di-, tri-, tetraallylsilane; the compounds were known and had been cyclopolymerized [14-17], and the polymerization activation energy per double bond had been determined [18, 19]. Progressive bathochromic shifts in the ultraviolet absorptions were observed. Series of related compounds were then considered to investigate possible explanations of the spectroscopic results.

RESULTS AND DISCUSSION

The spectroscopic data obtained in nonpolar and polar solvents and in the gas phase for allyltrimethylsilane (A1), diallyldimethylsilane (A2), triallylmethylsilane (A3), and tetraallylsilane (A4) are reported in Tables 2 and 3. Table 2 shows that, with increasing degree of allyl substitution, (i) a bathochromic shift occurs, (ii) the bathochromic shifts decrease asymptotically, (iii) the shifts are largest in the nonpolar solvent and

Table 2. Allylmethylsilanes, $\lambda_{\max}$ Values

	Isooctane			Ethanol			Gas phase		
Compound	$\lambda_{\max}$, mμ	Shift, mμ	Shift ratio	$\lambda_{\max}$, mμ	Shift, mμ	Shift ratio	$\lambda_{\max}$, mμ	Shift, mμ	Shift ratio
A1	192.3			193.6			188.7		
		2.4	1.00		1.9	1.00		1.0	1.0
A2	194.7			195.5			189.7		
		1.0	0.42		1.0	0.53		0.4	0.4
A3	195.7			196.5			190.1		
		0.5	0.21		0.5	0.26			
A4	196.2			197.0			[a]		

[a] Insufficient vapor pressure.

smallest in the gas phase, and (iv) the change in solvent from nonpolar to polar shifts the absorptions to a longer wavelength. Table 3 shows that, with increasing degree of allyl substitution, the extinction coefficients increase progressively but remain somewhat short of straight additivity.

Table 3. Allylmethylsilanes, Extinction Coefficients[a]

	Isooctane		Ethanol	
Compound	ϵ	ϵ ratio	ϵ	ϵ ratio
A1	10,566	1.0	9,150	1.0
A2	19,190	1.8	18,715	2.0
A3	28,840	2.7	27,616	3.0
A4	37,271	3.5	35,954	3.9

[a] Gas phase values could not be determined with sufficient accuracy.

A study of the structure of the molecules involved shows that possible causes for the shifts observed could be:

1. Structure modification due to replacement of methyl with allyl groups (two more carbons introduced each time).
2. Participation of the silicon d orbitals, leading to interaction with the allylic double bonds.
3. Interspatial, homoconjugative interaction of the type proposed for a cyclopolymerization mechanism.

Structure Modification

Every time that a methyl group is replaced with an allyl group in the compounds studied, the original structure is modified, because two more carbon atoms are introduced in each substitution. The fairly small value of the shifts obtained could support the objection that they could have been caused by the inductive effect of the lengthened alkyl chains. An examination of available ultraviolet data for homolog series, such as the values reported by Jones and Taylor [20] and Carr and Pickett [21-23] for unsaturated hydrocarbons, by Rice [24] for alkyl-substituted acetones, and by Matsen et al. [25] for monoalkyl-substituted benzenes, shows either negligible effects or the absence of regular trends in wavelength or extinction coefficients. A more definite answer, however, can be provided by the investigation of n-propylallylsilanes, where no structure change occurs on progressive allyl substitution.

The spectroscopic data obtained for allyltripropylsilane (A1P), diallyldipropylsilane (A2P), triallylpropylsilane (A3P), and tetraallylsilane (included for comparison) are reported in Tables 4 and 5. It is seen that the

Table 4. Allylpropylsilanes, λ_{max} Values [a]

	Isooctane			Ethanol		
Compound	λ_{max}, mμ	Shift, mμ	Shift ratio	λ_{max}, mμ	Shift, mμ	Shift ratio
A1P	194.5			194.9		
		1.3	1.00		1.3	1.00
A2P	195.8			196.2		
		0.6	0.46		0.8	0.61
A3P	196.4			197.0		
		0.3	0.23		0.4	0.31
A4[b]	196.7			197.4		

[a] The low vapor pressure of the allylpropylsilanes did not allow gas phase determinations.

[b] Run with the allylpropylsilanes for comparison.

Table 5. Allylpropylsilanes, Extinction Coefficients

	Isooctane		Ethanol	
Compound	ϵ	ϵ ratio	ϵ	ϵ ratio
A1P	10,129	1.0	9,670	1.0
A2P	18,626	1.8	17,715	1.8
A3P	27,343	2.7	26,347	2.7
A4[a]	37,271	3.7	35,954	3.7

[a] Run with the allylpropylsilanes for comparison.

observations made for the allylmethylsilanes apply also to the allylpropylsilanes, excluding structure effects as cause of the progressive bathochromic shifts obtained. Inductive effects due to the longer alkyl chains of the allylpropylsilanes, however, are probably responsible for the absorption of these compounds at slightly longer wavelength than the allylmethylsilanes. This effect is most marked, of course, for the first terms in the propyl series, so that the total shift A4-A1P becomes smaller than the corresponding A4-A1 shift of the methyl series.

Silicon d Orbitals Participation

The 3d orbitals of silicon can participate in $d\pi{-}p\pi$ bonding; the interaction can sometimes be observed as a bathochromic shift in the ultraviolet, due to the increased conjugation of the atoms. For example, a 7-mμ bathochromic shift of the main benzene absorption band was observed in mono- and tri-p-dimethylamino-substituted triphenylsilanols; this shift was ascribed [26] to resonance involving quinoid structures using silicon d orbitals; a moderate shift toward the visible (4.5 mμ) was also observed for the benzene absorption of phenyltrimethylsilane [27]. On the other hand, other phenylsilanes (triphenylsilane, triphenylsilanol, tetraphenylsilane) were found to absorb at the same wavelength as the corresponding carbon compounds [26].

The very diffuse silicon 3d orbitals could possibly extend far enough to overlap β,γ-conjugated systems [28] and interact with the allylic double bonds of allylmethylsilanes. The study of carbon analogs of the allylmethylsilanes (carbon replacing silicon), where no 3d involvement is possible, can verify this possibility. The spectroscopic data obtained for 4,4-dimethyl-1-pentene (A1C), 4,4-dimethyl-1, 6-heptadiene (A2C), and 4-allyl-4-methyl-1,6-heptadiene (A3C) are reported in Tables 6 and 7. The shifts obtained are now smaller but still follow the same trend observed

Table 6. Carbon Analogs of Allylmethylsilanes, λ_{max} Values

	Heptane			Acetonitrile			Gas phase[a]		
Compound	λ_{max}, mμ	Shift, mμ	Shift ratio	λ_{max}, mμ	Shift, mμ	Shift ratio	λ_{max}, mμ	Shift, mμ	Shift ratio
A1C	181.2			181.7			178.5		
		1.5	1.00		1.4	1.00		1.2	1.00
A2C	182.7			183.1			179.7		
		0.8	0.53		0.8	0.57		0.8	0.67
A3C	183.5			183.9			180.5		

[a] Gas phase shoulders, mμ: A1C, 172.6, 183.1, 189.7; A2C, 171.8, 184.6, 189.8; A3C, 182.5, 183.9, 190.1.

Table 7. Carbon Analogs of Allylmethylsilanes, Extinction Coefficients [a]

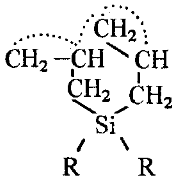
	Heptane		Acetonitrile	
Compound	ϵ	ϵ ratio	ϵ	ϵ ratio
A1C	11,629	1.0	9,576	1.0
A2C	22,138	1.9	19,893	2.1
A3C	31,000	2.7	30,055	3.1

[a] Gas phase values could not be determined with sufficient accuracy.

for the allylsilanes, excluding silicon d orbital participation as their cause. A comparison of the allylsilanes with the carbon analogs shows that the λ_{max} values of the allylsilanes are uniformly shifted toward the red of approximately 10 mμ: this shows that silicon participation is present, but appears to be independent of the degree of allyl substitution.

Interspatial Homoconjugation

In series of conjugated polyenes, one can observe how the increase in number of conjugated chromophores is accompanied by a corresponding increase in λ_{max} values and extinction coefficients, although the rate of increase diminishes as the number of conjugated chromophores becomes larger. This behavior is paralleled by the λ_{max} values and the extinction coefficients



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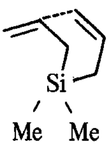

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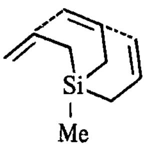

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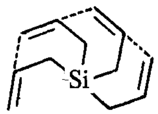


(VI)

observed for the allylsilane series. The bathochromic shift observed in allylsilanes with a change in solvent from nonpolar to polar is also observed for conjugated polyenes.

An interspatial, conjugative interaction in the allylsilanes could be represented by the general structure (III), which resolves into (IV), (V), and (VI) for A2, A3, and A4, respectively. Scale models show how a slightly offset p_σ interaction allows the formation of extended conjugated systems, such as the tricyclic structure (VI). The lower extent of interaction possible with a p_σ model could explain the fairly small value of the shifts obtained; the freedom of rotation of the allyl chains, reducing the probability of intramolecular interaction, could also be a factor.

The interaction depicted by structures (IV-VI) could be defined as a pseudobutadiene, pseudohexatriene, and pseudooctatetraene type. The frequency of ultraviolet absorption of conjugated polyenes and polyene aldehydes gives a linear correlation with the HMO (Huckel molecular orbital theory) energy difference between the highest occupied and the lowest unoccupied energy levels, corresponding to the most important π-π^* transition [30]. This energy difference (Δm) has been calculated for the pseudoolefins using a k value of 0.6 β for the partial bond (broken line in structures III-VI); this value is only meant to be indicative and was chosen after consideration of the k values used by other authors [29, 30] for p_σ interactions. The Δm value for ethylene (2.00) and the Δm values obtained from the calculations (pseudobutadiene, 1.48; pseudohexatriene, 1.26;

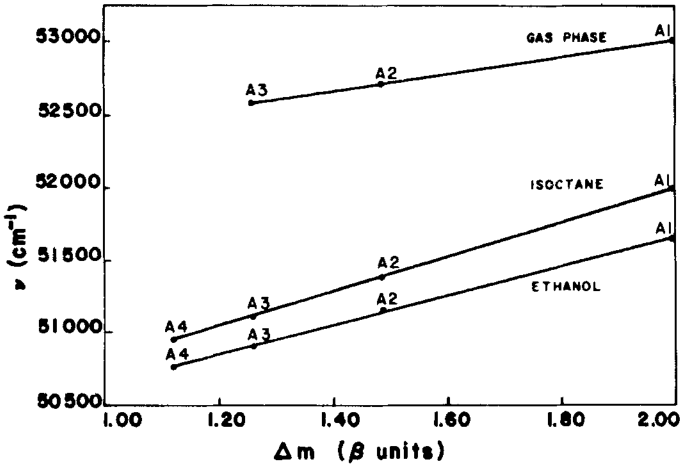


Fig. 1. Allylmethylsilanes, Δm-frequency correlation.

pseudooctatetraene, 1.13), were plotted in Fig. 1 versus the absorption frequencies of A1, A2, A3, and A4 in the various media. Straight lines were obtained in all cases.

Scale models of vinylmethylsilanes show that no interspatial, conjugative interaction of the type proposed for allylsilanes is possible. The ultraviolet behavior of these compounds was investigated. The data obtained for trimethylvinylsilane (V1), dimethyldivinylsilane (V2), trimethylvinylsilane (V3), tetravinylsilane (V4), and allyldimethylvinylsilane (AV) are reported in Tables 8 and 9. No regular trend was observed with increasing vinyl substitution, and the only significant feature was that V1 was shifted bathochromically from the rest of the vinylsilanes, which were grouped together. This provides further evidence for a conjugative interaction as cause of the shifts obtained for the allylsilanes, because other factors, such as structure effects and silicon participation, are still present in the vinylsilanes.

Table 8. Vinylmethylsilanes, λ_{max} Values mμ

Compound	Heptane	Acetonitrile	Gas phase
V1	178.5	179.3	177.5[a]
V2	177.7	178.7	175.8
V3	176.8	178.8	175.9
V4	176.9	178.6	175.2
AV	177.4, 193.9	177.7, 193.9	178.2, 190.8

[a] V1 gas phase shoulder: 175.6.

Table 9. Vinylmethylsilanes, Extinction Coefficients[a]

	Heptane		Acetonitrile	
Compound	ϵ	ϵ ratio	ϵ	ϵ ratio
V1	18,905	1.0	15,409	1.0
V2	28,395	1.5	25,553	1.6
V3	34,252	1.8	31,862	2.1
V4	38,553	2.0	36,520	2.4
AV[b]	20,433; 14,974		18,395; 13,817	

[a] Gas phase values could not be determined with sufficient accuracy.

[b] Same order as in Table 8.

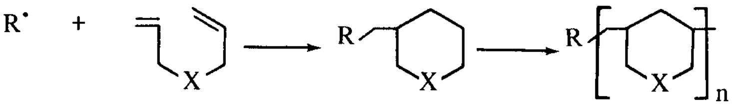
For another compound, allyldimethylvinylsilane (AV), an interspatial interaction appears highly strained and very unlikely. Its ultraviolet spectrum (Tables 8 and 9) shows that for both gas phase and solution, two independent absorptions were obtained, one in the vinylsilane region and one in the allylsilane region; interaction between the two unconjugated double bonds would have been expected to give one peak only or, at any rate, a spectrum different from the original components.

Cyclopolymerization

Polyallyl compounds are known to polymerize by an intra-intermolecular mechanism to give methylene-linked mono-, bi-, and tricyclic rings (from diallyl, triallyl, and tetraallyl monomers, respectively), as shown by Butler and Angelo [31] for various diallyl compound, Butler and Stackman [14] and Marvel and Woolford [15] for diallyldimethylsilane, Trifan and Hoglen [16] for triallylmethylsilane, and by Kropa [17] for tetraallylsilane.

4,4-Dimethyl-1,6-heptadiene (A2C) and 4-allyl-4-methyl-1, 6-heptadiene (A3C), new compounds, were cyclopolymerized using a Ziegler catalyst. The soluble polymers obtained melted at about 100°C, and had an inherent viscosity (25°C, 0.25%) of 0.06 and a residual unsaturation of 11% for poly(A2C) and 4.4% for poly(A3C) (from the $sp^2/[sp^2 + sp^3]$ hydrogen ratio of the NMR spectra). On the other hand, various attempts by Stackman [32] to cyclopolymerize allyldimethylvinylsilane were not successful; it has been seen that this compound gives no evidence of interaction in the ultraviolet spectrum.

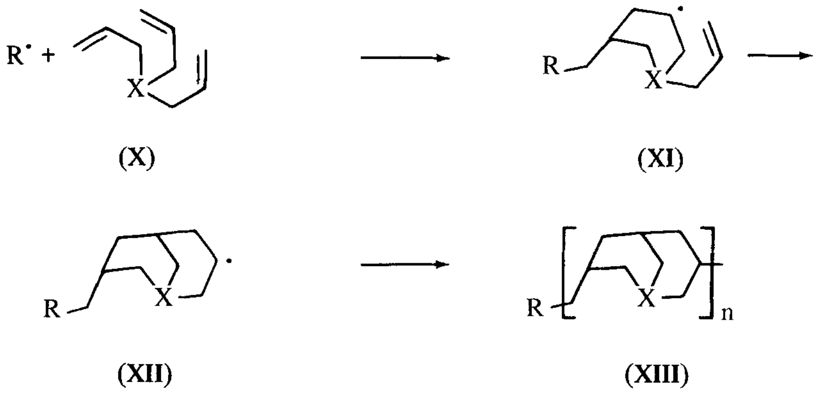
Butler and Angelo [31] proved that (IX) was the repeating unit in polymers obtained from diallyl systems, (VIII) being the transition state proposed (for free-radical initiators). Trifan and Hoglen [16] concluded from physical properties and hydrogenation studies of the polymers that



(VII) (VIII) (IX)

for triallyl derivatives, including triallylmethylsilane, polymerization occurred mainly through sequence **(X-XIII)** **(XI** and **XII** being the transition states), and that with tetraallyl derivatives, radical **(XII)** propagated once again intramolecularly to form a bridged tricyclic repeating unit. The low residual unsaturation value obtained for poly(A3C) supports these conclusions.

It is seen that the structures drawn for the cyclopolymerization transition states coincide with the sturctures depicting the interspatial, conjugative interaction proposed for the allylsilanes under ultraviolet excitation. The free-radical notation is only meant to be indicative, because, as shown by Field [33], for example, cyclopolymerization can occur by free-radical, anionic, or cationic mechanisms. The existence of this interspatial, conjugative interaction in the excited state of polyallyl systems could explain the very high intramolecular vs. intermolecular selectivity shown by these monomers in the repetitive cyclization steps.



(X) (XI)

(XII) (XIII)

According to the Franck-Condon principle [34, 35], conformation changes in molecules occur at a lower speed than electronic changes due to ultraviolet excitation. If the shifts observed are caused by an interspatial interaction, a conformation suitable for this interaction should preexist in the ground state, and the interaction would occur on call, under ultraviolet excitation or through the influence of the polymerization catalysts. At present, nuclear magnetic resonance and infrared data obtained for the compounds are inconclusive and do not support the occurrence of the interaction in the ground state.

A further possible confirmation of the identity of the transition state

Table 10. Activation Energies[a] Per Double Bond for the Polymerization of Allylmethylsilanes [18, 19]

Compound	E_a	E_a average	ΔE_a	ΔE_a ratio
A1	34-35	34.50		
			9.65	1.00
A2	24.5-25.2	24.85		
			4.35	0.45
A3	20-21	20.50		
			1.35	0.14
A4	18.8-19.5	19.15		

[a] kcal/mole.

of cyclopolymerization with the ultraviolet conjugative interaction proposed for the allylsilanes comes from kinetic studies by Mikulasova and Hrivik [18-19a] of the free-radical polymerization of A1, A2, A3, and A4. The authors found that the activation energy per double bond for the polymerization of the allylsilanes had the values reported in Table 10. It is seen that the ΔE_a ratios approach the shift ratios obtained from the ultraviolet spectroscopic study of the compounds.

CONCLUSIONS

The progressive bathochromic wavelength shifts observed in the ultraviolet spectra of allylmethylsilanes could not be due to structure effects from the progressive replacement of methyl with allyl groups, or to silicon d orbital participation, because the shifts were still observed in allylpropylsilanes, where no structure changes occur, and in carbon analogs of the allylmethylsilanes, where no 3d involvement is possible. Furthermore, no progressive bathochromic shifts were observed in vinylmethylsilanes, where silicon and structure effects are still present.

It is proposed that the progressive bathochromic shifts observed for the allylmethylsilane series are due to a homoconjugative, interspatial interaction between the double bonds, leading to pseudobutadiene, pseudohexatriene, and pseudooctatetraene structures. The conjugative character of the interaction is shown by similarity in the behavior of the spectroscopic data of allylsilane series and conjugated polyene series, and by a linear relationship between absorption frequencies and HMO Δm values

Table 11. Physical Properties of New Products Synthesized

Compound	Boiling point				Analytical				
					Calculated		Found		
	°C	Pressure, mm	n_D^{20}	d_4^{20}	C	H	C	H	Yield
Propionaldehyde diallyl acetal	85	45	1.4277	0.8713	69.19	10.32	69.27	10.32	68
2-Methyl-4-pentenal[a]	45	51	1.4204	0.8397	73.42	10.27	73.10	10.38	48
2-Methyl-4-pentenal diallyl acetal	99	19	1.4456	0.8797	73.43	10.27	74.28	10.37	63
2-Allyl-2-methyl-4-pentenal[a]	58	12	1.4482	0.8597	78.21	10.21	78.60	10.24	66
4,4-Dimethyl-1,6-heptadiene	63	90	1.4283	0.7427	87.01	12.98	87.19	12.83	76
4-Allyl-4-methyl-1,6-heptadiene	80	35	1.4553	0.7914	87.93	12.07	88.03	12.14	62

[a] 2,4-Dinitrophenylhydrazones: 2-methyl-4-pentenal, mp 101-102°C; 2-allyl-2-methyl-4-pentenal, mp 115-116°C.

for the pseudoconjugated structures postulated. Vinylmethylsilanes, where such structures could not be drawn, did not show any bathochromic shifts with increasing vinyl substitution; allyldimethylvinylsilane, where a conjugative interaction is highly unlikely, showed independent allyl and vinyl absorptions.

It is found that the structures drawn for the ultraviolet-excited state of the allylsilanes coincide with the structures postulated for the transition state of intra-intermolecular cyclopolymerization. All the allylmethylsilanes studied and the two new carbon analogs, 4,4-dimethyl-1,6-heptadiene and 4-allyl-4-methyl-1,6-heptadiene, have been cyclopolymerized to soluble polymers. The kinetic studies reported for the free-radical polymerization of allylmethylsilanes give activation energy ratios approaching the shift ratios obtained from the ultraviolet study.

EXPERIMENTAL

A nitrogen-flushed Beckman DK-2A spectrophotometer equipped with far ultraviolet silica optics and cells was used for the ultraviolet study. The solvents were chosen after measurement of their transparency in the range studied; with the exception of ethanol (technical, 95%), they were all of spectral grade. The compounds studied were redistilled materials, gas chromatographically pure; absorption vs. concentration plots showed full adherence to Beer's law; reproducible shift values were obtained for all compounds.

Allyltrimethylsilane, diallyldimethylsilane, trimethylvinylsilane, dimethyldivinylsilane, and tetravinylsilane were supplied by Peninsular ChemResearch, Inc.; and 4,4-dimethyl-1-pentene by Columbia Organic Chemicals. The remaining silanes were prepared by reaction of the halosilanes with allyl or vinyl Grignards, with the exception of diallyldipropylsilane, which required n-propyl lithium.

4,4-Dimethyl-1,6-heptadiene. This compound was prepared by Wolff-Kishner reduction [36] of 2-allyl-2-methyl-4-pentenal. The latter was obtained by a two-step rearrangement of propionaldehyde diallyl acetal, following a procedure outlined by Saunders [37] for similar compounds.

4-Allyl-4-methyl-1,6-heptadiene. This compound was obtained by a similar reduction of 2,2-diallyl-4-pentenal [38]. The physical properties of the new products synthesized are reported in Table 11; the analytical data were confirmed by the infrared spectra of the compounds (NMR spectra for the heptadienes).

Poly(4,4-dimethyl-1,6-heptadiene). A 125-ml Erlenmeyer flask was flamed out and flushed with nitrogen, then sealed with a rubber injection gasket. The flask was placed in a dry box (where the entire polymerization was carried out) and was injected in the following order: 15 ml of dry heptane, 6.4 ml of 1 M heptane solution of aluminum triethyl, 3.2 ml of 0.5 M heptane solution of titanium tetrachloride, and, after 1 min of shaking, 10 g (0.08 mole) of 4,4-dimethyl-1,6-heptadiene. After occasional shaking for 2 days, the reaction mixture was poured with stirring into 100 ml of methanol, then left to stand in the cold. Filtration yielded 1.1 g (11% conversion) of polymer, 0.7 g of which was soluble in benzene; after three reprecipitations from methanol, 0.4 g of white powder was obtained.

Poly(4-allyl-4-methyl-1,6-heptadiene). This was similarly prepared. The physical properties of the polymers have been reported above.

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