

Table VIII. Resolution of Racemic FP (MFP) by β -CD Complexation

sample	$[\alpha]_{365}$	c, g/mL	solvent	optical purity, ^a %
CD-MFP solution	-3.03	1.32	methanol	2.35
CD-MFP precipitate	+3.01	1.99	methanol	2.33

^a $[\alpha]_{365} + 129.22$ for (+)-(S)-FP (from Eli Lilly Laboratories).

has a cationic site that is responsible for the binding of the carboxylic acid group of arachidonic acid, and there is a hydrophobic surface and a hydrophobic pocket. The dimensions of the model active site of this enzyme are similar to those of β -cyclodextrin (Figure 1). Thus, it might be proposed that the steric restrictions imposed by fitting FP into a hydrophobic pocket in the enzyme may be similar to those experienced by the FP when fitting into the hydrophobic cavity of the β -CD. This could result in restricting the (*R*)-FP so that its carboxylic acid group points in the wrong direction for hydrogen bonding at the enzyme active site. Sallman also proposed that, for a biphenyl system to bind to the enzyme, the angle between the two aromatic rings should be $\sim 70^\circ$, and this corresponds to the interplanar angles of (*S*)-FP in the CD complex (Table VI).

Another cyclooxygenase active-site model proposed by Sankawa et al.²⁷ suggests that the carboxylic acid group of NSAIDS should bind and interact with the oxygenation site on the cyclooxygenase. This model requires an *S* configuration. Our results indicate that when the methyl group is positioned properly for hydrophobic interaction in the case of the *R* isomer of FP, the carboxylic acid group is then placed in an unfavorable position for hydrogen-bonding interaction. But for the *S* isomer, it would sit in a favorable hydrogen-bonding position on the enzyme.

Conclusions

In the crystal of the racemic FP- β -CD complex, the (*R*)- and (*S*)-FP guest molecules adopt different packing arrangements

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inside the β -CD dimer: *R* is head-to-head and *S* is head-to-tail, as had been found in the individual enantiomeric complexes. The differences of the packing between (*R*)- and (*S*)-FPs are due to effects such as the interior hydrophobicity of the β -CD cavity, the steric restrictions imposed by the tight fit of the guest inside the β -CD cavity, steric restrictions on the propionic acid substituent resulting in different orientations of the carboxylic acid group, and different ways of hydrating the carboxylic acid group.

In addition, the binding affinity of (*S*)-FP to β -CD is approximately 3 times stronger than (*R*)-FP due to the strong hydrogen bonds between the acid groups of (*S*)-FP and the β -CD secondary hydroxyl groups, which cannot be formed with (*R*)-FP. In the interface between the complex dimers, the methyl/phenyl interaction is more favorable for the (*S*)-FP complex than is the propionic acid/propionic acid interaction for the (*R*)-FP complex.

These effects result in β -CD preferentially selecting the *S* isomer of FP in the crystal form, which is confirmed by the change in specific rotation of the racemic FP- β -CD complex after complexation. This is the first crystal structure that supports the conditions for chiral recognition and resolution proposed by Armstrong. It also suggests models for the specificity of the enzyme cyclooxygenase for the *S* conformation of 2-arylpropionic acids.

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Registry No. β -CD-FP, 115245-44-8.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen positional parameters, individual bond lengths, and angles for CD molecules and hydrogen bonds involving water molecules (13 pages); observed and calculated structure factors (68 pages). Ordering information is given on any current masthead page.

Group Transfer Polymerization with Polyunsaturated Esters and Silyl Polyenolates

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Contribution No. 4352 from the Central Research and Development Department, E. I. Du Pont De Nemours and Co., Experimental Station, Wilmington, Delaware 19898. Received June 18, 1987

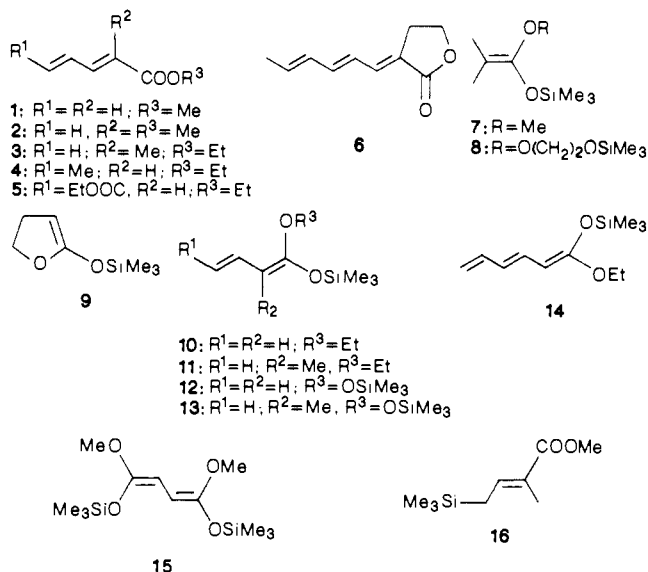
Abstract: The polyunsaturated monomers, methyl pentadienoate (**1**), methyl and ethyl 2-methylpentadienoate (**2** and **3**), ethyl sorbate (**4**), ethyl muconate (**5**), and 3-(2,4-hexadien-1-ylidene)-4,5-dihydrofuran (**6**) undergo group transfer polymerization (GTP). The reaction can be initiated by silyl ketene acetals or the silyl polyenolates **10-15** as well as the allylic silane **16** in the presence of a variety of nucleophilic anion catalysts. When silyl ketene acetals are used to initiate GTP of **1-3**, **5**, and **6**, control of \bar{M}_n is difficult, and polymers with \bar{M}_n much higher than theory are obtained. \bar{M}_n closer to theory and low polydispersity are achieved by initiation with silyl polyenolates. Regiospecific 1,4-polymerization occurs with the diene monomers, and 1,6-polymerization occurs with the triene lactone **6**. GTP of ethyl sorbate and ethyl muconate proceeds with 2:1 erythro and 2:1 meso selectivity and 3:1 trans-cis geometry of the backbone double bond. The triene lactone **6** appears to show no diastereoselectivity but high trans selectivity with respect to double-bond geometry. The unsubstituted silyl dienolates **10** and **12** and the silyl trienolate **14** show regiospecific initiation of GTP of MMA at the 2-position. The 2-methyl diene homologues **11** and **13** show regioselective initiation of GTP of MMA at the 2-position, with about 28% initiation at the 4-position.

The rapid growth of interest in regio- and stereoselective synthesis of acyclic molecules during the past decade has led to a remarkable focus upon the use of organosilicon compounds,

particularly silyl enolates, in carbon-carbon bond-forming reactions. A notable result of the extension of the study of the carbon-carbon bond-forming reactions of silyl ketene acetals with

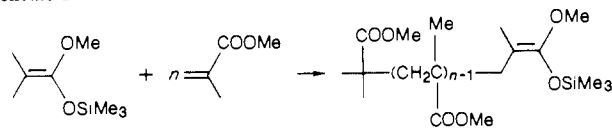
Michael-type electrophiles was the discovery¹ of group transfer polymerization (GTP). This process, which is undergoing commercial development, is illustrated for methyl methacrylate (MMA) in Scheme I. The major factors that control the stereochemistry of MMA polymerization by anion-catalyzed GTP have been elucidated.^{1c,2,3}

The question of regio- and stereochemical control of reactions of silyl polyenolates has also been receiving increasing attention because of the importance of controlled synthesis of unsaturated compounds. Most of these studies have focused on reactions of silyl polyenolates with simple electrophiles.^{4,5} We have recently elucidated the regiochemistry and stereochemistry of reactions of silyl dienolates with aldehydes.⁴ However, the problem of regiochemistry of carbon-carbon bond-formation in anion-catalyzed Michael addition reactions with α,β -unsaturated carbonyl compounds and polyunsaturated carbonyl compounds has not yet been addressed. In this paper we address these problems as well as the more complex problem of stereochemistry of the resulting unsaturated GTP polymers. We also examine these problems in the context of the much better understood GTP of simple unsaturated esters.^{1c} The study includes GTP of methyl pentadienoate (**1**), methyl 2-methylpentadienoate (**2**), ethyl 2-methylpentadienoate (**3**), ethyl sorbate (**4**), ethyl muconate (**5**), and the triene lactone 3-(2,4-hexadien-1-ylidene)-4,5-dihydrofuran (**6**). Silyl ketene acetals **7**, **8**,^{1c} and **9**;⁶ the silyl polyenolates 1-ethoxy-1-(trimethylsilyloxy)-1,3-butadiene (**10**), 1-ethoxy-2-methyl-1-(trimethylsilyloxy)-1,3-butadiene (**11**), 1,1-bis(trimethylsilyloxy)-1,3-butadiene (**12**), 1,1-bis(trimethylsilyloxy)-2-methyl-1,3-butadiene (**13**), 1-ethoxy-1-(trimethylsilyloxy)-1,3,5-hexatriene (**14**), and 1,4-dimethoxy-1,4-bis(trimethylsilyloxy)-1,3-butadiene (**15**); and the silyl ester methyl 2-methyl-4-(trimethylsilyl)but-2-enoate (**16**) were used as initiators. For the structural analyses we have used, primarily, multinuclear NMR techniques.

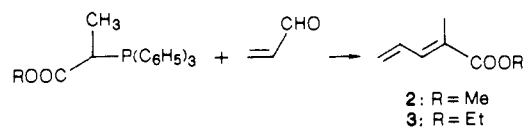


Synthesis. Two of the monomers, ethyl sorbate (**4**) and methyl pentadienoate (**1**), are commercially available. The methyl and ethyl esters of 2-methylpentadienoic acid (**2** and **3**) were prepared by the general procedure of House and Rasmussen⁷ (Scheme II).

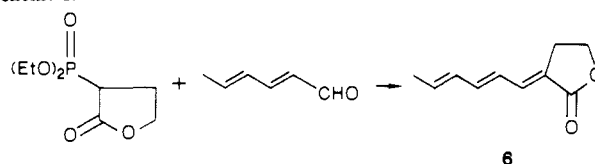
Scheme I



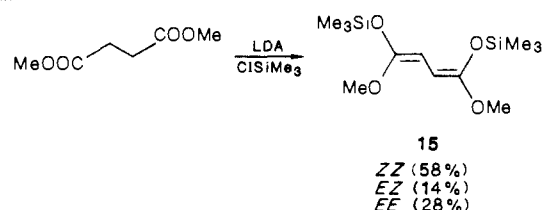
Scheme II



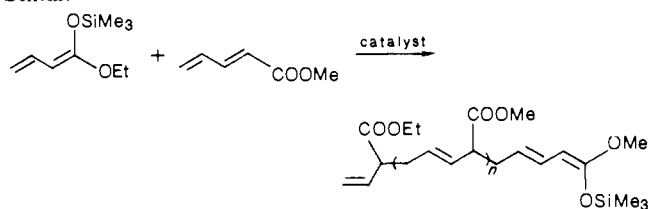
Scheme III



Scheme IV



Scheme V



Triene lactone **6** was synthesized by a Michaelis-Arbuzov reaction of 2-(diethylphosphono)-4-butyrolactone⁸ with sorbaldehyde (Scheme III) and isolated as a sublimable crystalline compound with mp 99.5–100.5 °C. ¹H NMR analysis indicates that the geometry is all trans. Diethyl muconate (**5**) was prepared by esterification of commercially available muconic acid.

The silyl ketene acetals **7–9** were prepared by using standard literature procedures.^{1c,6} The silyl dienolates **10** and **11** were prepared by methods described in an earlier study,⁴ which provided the compounds with equilibrated geometry consisting of 90% *Z* and 67% *Z*, respectively, and **12** was prepared as described by Bellassoued and Gaudemar⁹ from the reaction of lithium diisopropylamide (LDA) and chlorotrimethylsilane with vinylacetic acid. 1,1-Bis(trimethylsilyloxy)-2-methyl-1,3-butadiene (**13**) was prepared by the reaction of LDA and chlorotrimethylsilane with tiglic acid. The silyl trienolate **14**, synthesized as described earlier,^{4,10} was obtained as the equilibrated mixture of geometric isomers, 95% *Z,E*, 5% *E,E*. The reaction of dimethyl succinate with LDA and chlorotrimethylsilane, in a modification of the procedure of Long and Rathke,¹¹ gave a mixture of three isomers of 1,4-dimethoxy-1,4-bis(trimethylsilyloxy)-1,3-butadiene (**15**) as shown in Scheme IV. The stereochemistry of the ester **16** has not been proved.⁴

Treatment of the conjugated polyolefinic esters **1–6** with a silyl ketene acetal or silyl polyenolate and a catalytic amount of bi-

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Table I. Group Transfer Polymerization of Esters of Polyenoic Acids^a

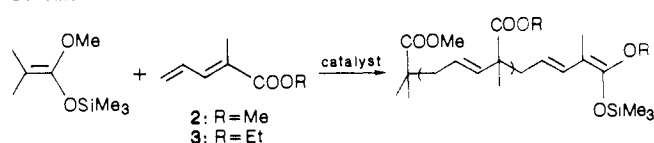
entry	monomer, mmol	init., mmol	cat., μ mol	temp, °C	\bar{M}_n (theory)	\bar{M}_n	\bar{M}_w	<i>P</i>	<i>T_g</i> , °C
1	1, 50	10, 1.0	Bu ₄ NOAc, 1	-1 to 34	5700	6690	10 300	1.54	
2	1, 25.7	9, 0.25	TASF, ^b 250	-78 to -40	4000	10 000	22 000	2.2	
3	1, 25	7, 0.5	Bu ₄ NOAc, 1	13 to 45	5700	37 000	123 000	3.3	1.6
4 ^c	2, 60	13, 1.0	Bu ₄ N <i>m</i> CB, ^d 6	35	7700	11 800	15 000	1.27	
5 ^c	2, 60	10, 1.0	Bu ₄ N <i>m</i> CB, 5	35	7700	11 800	16 000	1.35	
6 ^c	2, 60	7, 1.0	Bu ₄ N <i>m</i> CB, 5	35	7700	33 900	61 400	1.81	
7	2, 50	15, 1.0	Bu ₄ N <i>m</i> CB, 7.5	35	6400	25 700	41 200	1.60	
8	2, 47	10, 0.25	TASHF ₂ , ^e 4	-75 to -69	23 800	34 900	48 000	1.37	
9	2, 50	10, 0.25	TASHF ₂ , 1	25 to 42	25 200	46 500	58 700	1.26	3
10	3, 28.5	7, 0.25	TASHF ₂ , 10	25 to 52	16 000	52 200	228 000	4.33	-27
11	4, 50	7, 0.5	Bu ₄ N <i>m</i> CB, 6	25 to 35	14 100	18 700 ^f	36 300	1.97	7
12	5, 10.1	10, 1.0	Bu ₄ N <i>m</i> CB, 10	28 to 39	2000	1850	3330	1.80	
13	5, 35.3	10, 1.25 ^g	Bu ₄ N <i>m</i> CB, 10	25 to 35	>5800	14 000	33 500	2.39	15
14	6, 5.0	7, 5.0	Bu ₄ NOAc, 14	25 to 27	264	7240 ^h	10 900	1.51	150

^a Polymerizations were carried out in tetrahydrofuran solution either by a batch process (all of the monomer present at the start of the polymerization), which produced the indicated temperature rise, or by a feed process in which monomer was added at a rate to maintain the indicated temperature. All yields of polymer were quantitative except for entry 2 in which the yield was 36%. The values for \bar{M}_n and \bar{M}_w were determined by gel-permeation chromatography with PMMA standards. ^b TASF is tris(dimethylamino)sulfonium difluorotrimethylsilicate; TASHF₂ is tris(dimethylamino)sulfonium bifluoride. ^c After addition of the first 30 mmol of monomer, GPC showed \bar{M}_n 4950, \bar{M}_w 6330, *P* = 1.28 (theory, \bar{M}_n 4000) for entry 4; \bar{M}_n 8440, \bar{M}_w 9950, *P* = 1.18 (theory, \bar{M}_n 3900) for entry 5; and \bar{M}_n 28 300, \bar{M}_w 53 100, *P* = 1.88 (theory, \bar{M}_n 3900) for entry 6. The reaction mixtures were allowed to stand for 1 h before beginning the addition of the final 30 mmol of monomer. Conversions in both steps were quantitative. \bar{M}_n as determined by vapor phase osmometry (VPO) in toluene is 10 400 for final product in entry 5. ^d Bu₄N*m*CB is tetrabutylammonium *m*-chlorobenzoate. ^e Addition of 25 mmol of 4 to the reaction mixture after 1 h resulted in further polymerization with consumption of 35% of the additional monomer charged. GPC analysis showed an increase in molecular weight, \bar{M}_n 29 800, \bar{M}_w 58 800, *P* = 1.97. \bar{M}_n as determined by VPO in toluene is 24 500. ^f Initiator, 10, was added in 0.25-mmol increments to titrate impurities in the monomer until slow polymerization began. A total of 1.25 mmol of 10 was required, but the amount of 10 actually involved in initiation is less than 1.25 mmol, hence, an exact value for the theoretical \bar{M}_n is not known. ^g This molecular weight data is not representative of the entire polymer, since part of the product precipitated from the reaction solution. This data was obtained from the "insoluble" fraction. The chromatographic measurements were performed on a THF solution of the polymer following filtration to remove some insoluble material.

fluoride or carboxylate salt² led to polymerization of the esters. The conversions to polymer were, in most cases, quantitative. The results are summarized in Table I.

Polymerization of Methyl Pentadienoate (1). Free-radical^{12a-c} and anionic^{12d} polymerization of esters of pentadienoic acid and free-radical polymerization of pentadienoic acid¹³ have been reported to occur in a 1,4 fashion, producing a trans carbon-carbon double bond. GTP of 1 with initiation by 10 and catalysis by tetrabutylammonium acetate² at 0 °C gave a quantitative yield of poly(methyl pentadienoate) \bar{M}_n 6690 (theory, \bar{M}_n 5700) and a polydispersity of 1.54 (Table I, entry 1; Scheme V). The reasonably good agreement between the observed \bar{M}_n and the \bar{M}_n projected by the ratio of monomer to initiator is consistent with a rate of initiation by 10, which is no slower than the rate of propagation.^{1c} In contrast, GTP of 1, whether initiated by the silyl ketene acetal 9 with catalysis by tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) at low temperature or by the silyl ketene acetal 7 with catalysis by acetate at room temperature, produced polymer with relatively high polydispersity (Table I, entries 2 and 3). High conversion to polymer was more readily obtained in a batch process than in a monomer-feed process. The apparent loss of some living ends may be due to chain transfer to polymer, which has been suggested as the cause of similar behavior in GTP of acrylates.^{1c} The observed \bar{M}_n with initiators 7 and 9 was substantially higher than theory and higher than the \bar{M}_n obtained with 10 as initiator. This, together with the high polydispersity, suggests that the rate of initiation by 7 and 9 is lower than the rate of propagation. Similar instances of low rates of initiation relative to rates of propagation leading to poor control of molecular weight in GTP have been reported earlier for methacrylates with certain types of initiators.^{1c} Thus, much better control of \bar{M}_n is achieved with initiator 10, which structurally resembles the living end group in GTP of 1, than with the silyl ketene acetals 7 or 9.

Scheme VI



Since the values of \bar{M}_n determined by GPC by using PMMA standards are generally somewhat higher than theory, not only for poly-1, but for the other polymers prepared in this study, it became important to determine the appropriateness of using PMMA as a standard for these unsaturated polymers. Yau et al. recently reported the use of a capillary visometer as a continuous detector for size-exclusion chromatography along with a universal calibration technique.¹⁴ We applied this method to the sample of poly-1 described in Table I, entry 1 with the following results: \bar{M}_n 8230, \bar{M}_w 9700, *P* = 1.18, $[\eta]_{\text{THF}}$ 0.115. The results using this method agree reasonably well with the GPC measurements using PMMA standards, particularly considering the relatively low molecular weight of the sample. The universal calibration method gives a lower polydispersity value (1.18 vs 1.54). Thus, GPC values based on PMMA standards probably provide a reasonable representation of the molecular weights of the unsaturated polymers of this study.

The infrared spectrum of poly(methyl pentadienoate) shows absorption at 970 cm⁻¹ consistent with a trans double bond. ¹³C NMR analysis shows an unusual coincidence of the resonances of the two olefinic carbons consistent with the double bond being internal rather than pendent to the backbone (Scheme V). The proton-decoupled resonance signals of all of the carbons are single peaks, which eliminates the possibility of appreciable quantities of cis carbon-carbon double bonds, but which also allows no information on tacticity to be inferred from the ¹³C NMR spectrum. The resulting poly-1 is a viscous liquid with *T_g* 1.6 °C. Upon prolonged storage, samples of the polymer became cross-linked and insoluble.

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Polymerization of Methyl and Ethyl 2-Methylpentadienoate (2 and 3). Methyl and ethyl 2-methylpentadienoate (**2** and **3**) were polymerized for the first time with GTP. GTP of **2** gives living polymer, which can be held in the reaction mixture for 1 h after the addition of monomer has been stopped, and, upon addition of more monomer, undergoes further polymerization with increase in molecular weight (Table I, entries 4–6). Presumably the 2-methyl group contributes to the stability of the living polymer by preventing the kind of chain transfer¹⁵ to polymer processes, which have been proposed¹⁶ to occur during GTP of acrylates and which may occur in GTP of **1**. Initiation of GTP of **2** or **3** with the silyl ketene acetal **7** (Scheme VI; Table I, entries 6 and 10) produces polymer with a much higher \bar{M}_n than theory and a high polydispersity. When the same polymerization is initiated with the silyl dienolate **13**, the observed \bar{M}_n , 4950, is close to theory (4000), and the polydispersity is only 1.28 (see Table I, footnote c). Initiation of GTP of **2** with silyl dienolate **10** gives results similar to those obtained with **13**, although the initial \bar{M}_n (8440) is higher than theory (Table I, entry 5, footnote c). The superior results of initiation by silyl dienolates may be explained by the fact that initiation of polymerization of **2** by the silyl ketene acetal **7** is slow relative to propagation, while the rate of initiation by the silyl dienolates **10** and **13** are at least comparable to the rate of propagation. In contrast to the GTP of **2** initiated with **10** or **13**, initiation with **15** gave poor control of molecular weight (Table I, entry 7). The rate of initiation by **15** may be slower than that by **10**. Initiation of GTP of **2** with **10** and TASHF₂ at -75 to -69 °C gave results similar to the same system at ambient temperature (Table I, entries 8 and 9). Because of the slower rate of polymerization at low temperature, more catalyst was used to obtain a convenient rate. Both poly-**2** and poly-**3** were obtained as viscous liquid polymers. The T_g of poly-**2** is 3 °C, and that of poly-**3** is -27 °C, which is the lowest of any of the polymers in this study. The ¹H NMR spectra of both polymers clearly show that 1,4-polymerization has occurred to the exclusion of any detectable 1,2-polymerization, and the carbon-carbon double bond in the polymer chain has *E* geometry. The ¹³C NMR spectrum of poly-**3** shows only single resonances for each carbon in the repeat unit, thus providing no information on tacticity. The NMR data for poly-**3** are detailed in the Experimental Section.

The \bar{M}_n values measured for samples of poly-**2** by GPC with PMMA standards were invariably higher than the values expected from consideration of the ratio of monomer to initiator, in spite of the well-behaved nature of this living polymerization. This may be due to the loss of some initiator from fast side reactions, which do not affect the less reactive living end of polymer. To confirm the validity of the GPC molecular weight values, the GPC-viscosity-universal calibration method of Yau et al.¹⁴ was used for analysis of the polymer sample of Table I, entry 4, with the following results: \bar{M}_n 13 000, \bar{M}_w 14 300, $P = 1.10$, $[\eta]_{\text{THF}}$ 0.133, in excellent agreement with the results obtained from GPC with PMMA standards.

Polymerization of Ethyl Sorbate (4). Natta and co-workers^{16a-c} have described the anionic polymerization of esters of sorbic acid, including ethyl sorbate, which produced crystalline stereoregular erythro diisotactic polymers. GTP of **4** appeared to be slower than GTP of **1-3**. Initiation of polymerization of **4** with the silyl ketene acetal **7** resulted in good control of \bar{M}_n contrasting the lack of control of \bar{M}_n with **1-3** when initiated by **7**. Thus, the observed \bar{M}_n (18 700) was only 33% higher than theory (14 100, see Table I, entry 11). The polydispersity was high at 1.97. We attribute the good control of \bar{M}_n to the reduced rate of propagation, which results from the steric hindrance at C-5 in the transition state for addition of living polymer end. Thus, the rate of propagation is

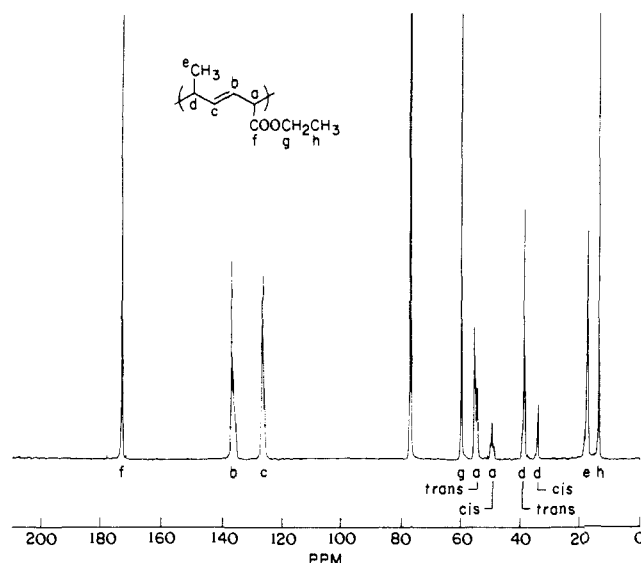
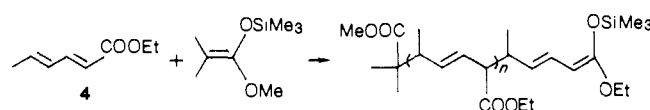


Figure 1. 100.6-MHz ¹³C NMR spectrum of poly(ethyl sorbate) prepared by GTP (solvent, CDCl₃).

Scheme VII



comparable to the rate of initiation by **7**, which is inherently slower than initiation by a silyl polyenolate, such as **10**. The high polydispersity is attributed to slow chain transfer to polymer due to the presence of a hydrogen atom adjacent to the ester group in the polymer.^{1c}

Poly-**4** was obtained by GTP as a viscous liquid polymer with a T_g of 7 °C (Scheme VII). This is in marked contrast to the crystalline (mp 175 °C) poly-**4** obtained by anionic polymerization.^{16a} Absorption at 975 cm⁻¹ in the infrared spectrum confirms a predominant *E* configuration for the double bond. ¹H NMR spectroscopy shows that the resonance of the backbone methyl group occurs at 0.9 ppm, characteristic of a methyl group on a saturated carbon rather than a vinylic carbon. This excludes the possibility of any 1,2-polymerization. The 1,4-structure of poly-**4** prepared by GTP is analogous to that of the polymer prepared by anionic polymerization.^{16a-c}

Ethyl sorbate is the first example of a monomer that generates two adjacent chiral centers during the propagation step of GTP. Therefore, it is of special importance to determine the diastereoselectivity, if any, of the process. The lack of stereoregularity in poly-**4** is apparent from the complexity of both methyl resonances in the 400-MHz ¹H NMR spectrum. A 2D-J resolved NMR experiment was also carried out. The backbone methyl resonance is very complex, even though the methine couplings have been removed by the 2D-J experiment, consistent with erythro-threo and tactic inhomogeneity.

The ¹³C NMR spectrum of poly-**4** made by GTP provides more specific information on the stereochemistry. Figure 1 shows the ¹³C NMR spectrum of poly-**4** with peak assignments. A spin-echo experiment with gated decoupling caused inversion of the resonances of carbons bearing an odd number of hydrogen atoms. The resonances labeled a–e and h (Figure 1) were inverted, consistent with the assignments. The general features of the ¹³C NMR spectrum of poly-**4** made by GTP are in good agreement with the spectrum of poly(methyl sorbate) made by anionic polymerization and reported by Farina,^{16d} except for the presence of the two resonances labeled cis-a and cis-d, which were not reported by Farina. We attribute these resonances to the methine carbons a and d adjacent to cis carbon-carbon double bonds. The resonances labeled trans-a and trans-d are attributed to methine carbons adjacent to trans double bonds. The fact that the only carbons that show appreciable chemical shift differences in the

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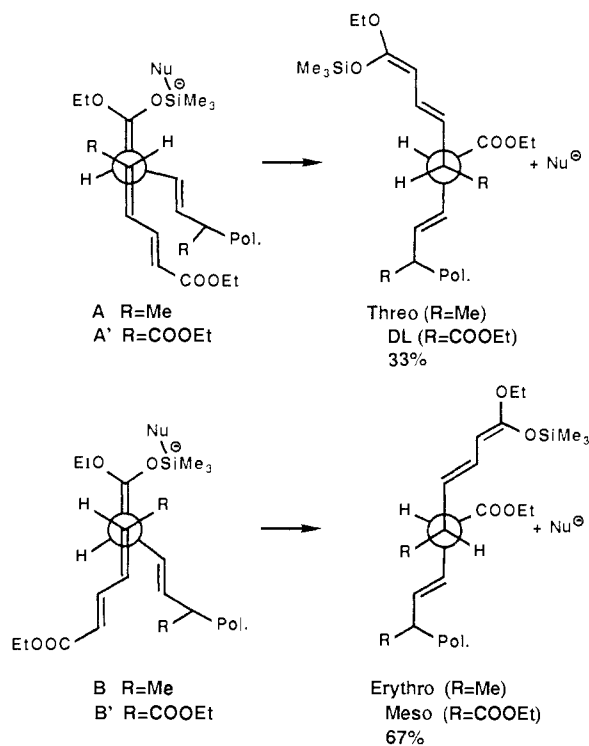
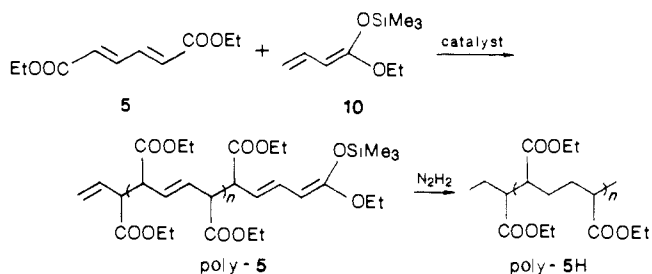


Figure 2. Antiperiplanar transition states leading to threo and erythro poly(ethyl sorbate) and *dl* and meso poly(ethyl muconate). Silyl enolates are arbitrarily depicted as *Z* isomers only because this is the thermodynamically more stable configuration in the analogous silyl dienolate, **10**.⁴

cis and *trans* repeat units are the carbons adjacent to the double bonds (carbons a and d in Figure 1) is consistent with the studies of Dorman, Jautelat, and Roberts,¹⁷ who found that the resonances of carbons 1 and 4 in *cis*-2-hexene were shifted 5.1 and 5.9 ppm to high field of carbons 1 and 4 of *trans*-2-hexene. None of the other resonances of the two isomers differed by more than 1.1 ppm. Similar results were reported for *trans*- and *cis*-3-hexene and *trans*- and *cis*-4-octene.¹⁷ In the spectrum of poly-**4**, the chemical shift differences between *trans*-a (55.5 ppm) and *cis*-a (50.1 ppm), and between *trans*-d (39.6 ppm) and *cis*-d (34.5 ppm) are 5.4 and 5.1 ppm, respectively. The ratio of the intensity of *trans*-a:*cis*-a and *trans*-d:*cis*-d is 3:1. Thus, the ratio of *trans* to *cis* carbon-carbon double bonds in poly-**4** is 3:1. Poly(methyl sorbate) prepared by GTP showed a 3.5:1 ratio of *trans* to *cis* carbon-carbon double bonds (see the Experimental Section).

Farina and co-workers^{16d} and Corradini and co-workers^{16e} have extended the earlier work^{16a,b} on anionic polymerization of sorbates and reported new ¹H and ¹³C NMR and X-ray studies on two semicrystalline forms of poly(methyl sorbate) prepared (a) by initiation with butyllithium in toluene to give predominantly erythro (60%), *trans*, diisotactic polymer and (b) by initiation with butyllithium-tetramethylurea in toluene to give predominantly threo (75%), *trans*, diisotactic polymer. Both polymers lacked the methine resonances observed in the *cis* repeat units of poly-**4** and poly(methyl sorbate) made by GTP. The erythro and threo ¹³C NMR assignments were reported for the polymers made by anionic techniques, as well as the saturated polymers prepared by diimide reduction.^{16d} Since the presence of 22–25% of *cis* units in our polysorbates made erythro and threo assignments somewhat uncertain, poly-**4** and poly(methyl sorbate) were reduced with diimide. Comparison of the ¹³C NMR spectra of both saturated polymers with the spectra of the reduced poly(methyl sorbates) reported by Farina^{16d} shows the stereochemistry of both of our reduced polymers to be 2:1 erythro:threo (see the Experimental Section). Thus, the erythro diastereoselectivity in GTP of **4** and methyl sorbate is similar to that of anionic polymerization of

Scheme VIII



methyl sorbate (toluene, butyllithium).^{16d} Principal differences are the 25% *cis* repeat units produced by GTP, which are not observed in anionic polymerization, and the greater tactic irregularity in the polymers made by GTP. The tactic irregularities are apparent in the fine structure within the erythro and threo resonances of the reduced GTP polymers. These factors may account for the observed physical differences between the anionic and GTP polymers.

If we now consider the erythro and threo structures generated by a propagation step in GTP of **4**, as shown in Figure 2, there is a greater number of nonbonded interactions in the threo adduct than in the erythro adduct. If we assume that the same ordering of interactions will obtain in the diastereomeric centers upon extension of the living end to higher polymer, then this analysis is in agreement with that of Natta and co-workers,^{16a} who conclude that steric interactions are greater in threo poly-**4** than in erythro poly-**4**. Thus, GTP of **4** produces an excess of less hindered diastereomeric units. Examination of molecular models of the antiperiplanar⁵ transition states (A and B in Figure 2) leading to the threo and erythro diastereomers show that there are fewer unfavorable nonbonded interactions in B than in A. Although another conformer of A appears to be of lower energy than A and appears, from examination of the molecular models, to be comparable in energy to B, the fact that the predominant product is the erythro diastereomer suggests that both diastereomers result from the antiperiplanar transition states, A and B. If dissociation of the silicon occurs before carbon-carbon bond formation, the same arguments apply to the corresponding transition states derived from the naked dienolates.

Polymerization of Diethyl Muconate (5). Anionic polymerization of **5** with butyllithium in toluene has been reported¹³ to produce a solid polymer in 35% yield. GTP of **5** with initiation by **10** and tetrabutylammonium *m*-chlorobenzoate catalyst gave a quantitative yield of poly-**5** as a tacky polymer with *T_g* 15 °C (Scheme VIII; Table I, entries 12 and 13). Although the number average molecular weight is controlled by the ratio of monomer **5** to initiator **10**, the polydispersity is high. The polydispersity of a higher molecular weight polymer (Table I, entry 13) is greater than that of a lower molecular weight polymer (Table I, entry 12), suggesting that the α -hydrogen atoms of the polymer backbone may be implicated in a slow (relative to propagation rate) chain transfer¹⁵ process as has been proposed to occur in GTP of acrylates.^{1c}

The low *T_g* of poly-**5** suggests a lack of stereoregularity in the polymer. The infrared spectrum of the polymer shows absorption at 970 cm⁻¹, characteristic of a carbon-carbon double bond with *trans* geometry, and 1732 cm⁻¹, characteristic of an unconjugated ester C=O. The resonances in the ¹H NMR spectrum are quite broad, and the absence of any resonance at lower field than 5.53 ppm precludes the presence of any protons on a double bond conjugated to an ester. Thus, the poly-**5** is formed by 1,4-polymerization, and the backbone double bond is predominantly *trans* (see Scheme VIII).

The ¹³C NMR spectrum (Figure 3) provides valuable stereochemical information. The resonances of the saturated backbone carbon atoms appear as two well-separated multiplets centered at 50.9 and 46.1 ppm (labeled d in Figure 3). These resonances can be assigned to methine carbons α to *trans* and *cis* carbon-carbon double bonds, respectively. The magnitude of the high-field chemical shift for the methine resonance of the *cis* repeat unit

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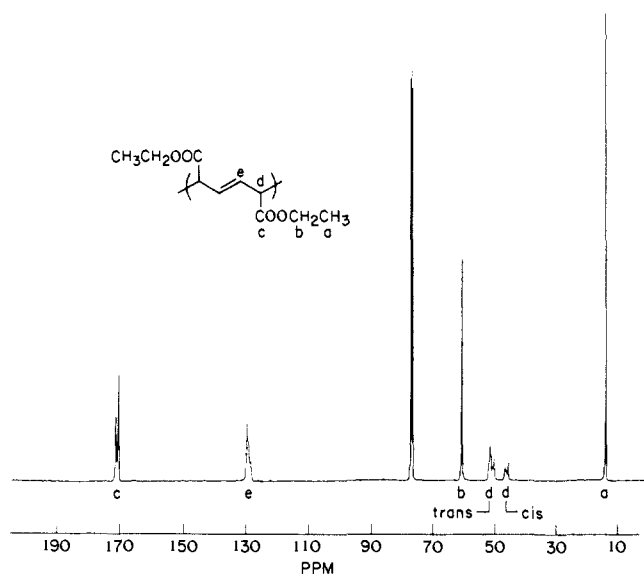


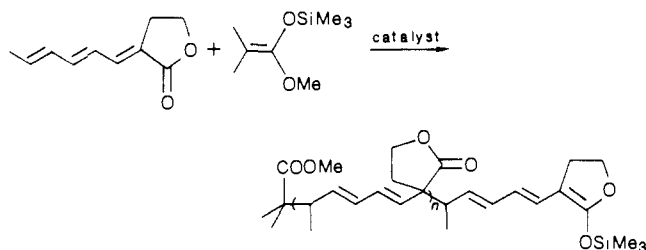
Figure 3. 100.6-MHz ^{13}C NMR spectrum of poly(ethyl muconate) prepared by GTP (solvent, CDCl_3).

(4.8 ppm) is consistent with the literature¹⁷ and with our findings for poly-4 and poly(methyl sorbate). In order to quantify the integration of the resonances due to *trans* and *cis* methine carbons, a ^{13}C NMR experiment was performed at a 45° tilt angle with gated decoupling to suppress the Overhauser effect, and the time between pulses was set at 10 s to remove the possibility of different saturations. This experiment shows that there are three times as many *trans* units as *cis* units in the polymer backbone, the same ratio found in poly-4.

In order to determine the diastereoselectivity, if any, in GTP of 5, the polymer was subjected to hydrogenation with diimide to remove the structural inhomogeneities due to double-bond geometry (Scheme VIII). The resulting polymer, poly-5H, is formally the alternating copolymer of ethylene and diethyl maleate, a structure confirmed by ^1H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of poly-5H shows paired resonances for the two backbone carbons and the carbonyl carbon due to the presence of meso and racemic units. The largest of the chemical shift differences (1.39 ppm) is seen in the backbone methylene resonance. Literature precedent¹⁸ shows that the resonances for the diastereotopic carbons can be used to distinguish meso from racemic compounds, since the meso resonance typically occurs to low field of the racemic resonance. Rätzsch et al.¹⁹ have made the meso and racemic ^{13}C NMR assignments in the alternating copolymer of ethylene and maleic acid. The meso CH_2 , CH , and $\text{C}=\text{O}$ resonances were reported to be 29.9, 48.6, and 174.9 ppm, and the corresponding racemic resonances, 26.6, 46.7, and 176.1 ppm.^{19a} Using this model, we can assign the 28.06, 47.88, and 173.13 ppm resonances of poly-5H to meso CH_2 , CH , and $\text{C}=\text{O}$, and the 26.63, 46.77, and 173.24 ppm resonances to the corresponding racemic carbons. From the intensities of the meso and racemic CH_2 and CH resonances it is apparent that the meso:racemic ratio in poly-5H, hence in poly-5, is about 2:1.

The stereochemical relationships between poly-5 and poly-4 prepared by GTP are shown in Figure 2. The 2:1 meso selectivity in GTP of 5 reproduces the 2:1 erythro selectivity displayed in GTP of 4. Clearly, the same factors in the transition states or products that are stereochemical determinants in polymerization of 4 are operative (and apparently to the same degree) in the polymerization of 5. It is particularly interesting that the 2:1 diastereoselective formation of the more stable polymer in the GTP

Scheme IX



of 4 and 5 parallels the 3:1 1,3-diastereoselective generation of *r* dyads (relative to *m* dyads) in GTP of MMA at similar reaction temperatures.^{1c} It would be of interest to measure the temperature-dependence of diastereoselectivity in the GTP of 4 and 5 as has been done in GTP of MMA^{1c} and in reactions of 10 with aldehydes.⁴

Polymerization of 6. GTP of the triene lactone 6 appears to be the first example of polymerization of a conjugated triene ester. The anionic polymerization of hexatriene has been reported to form a mixture of *cis*- and *trans*-1,2-, 1,4-, and 1,6-poly(hexatriene).²⁰ Surprisingly, treatment of the triene lactone in THF solution with 1 equiv of silyl ketene acetal 7 in the presence of a catalytic quantity of tetrabutylammonium acetate led to polymerization to fairly high molecular weight (Table I, entry 14, Scheme IX). This dramatically demonstrates the inefficiency of initiation of this monomer with a silyl ketene acetal. The poly-6 partly precipitated from the reaction medium, the higher molecular weight fraction of the polymer being relatively insoluble in THF. Both the soluble and insoluble fractions of polymer were solids. The polymer is largely insoluble in THF and toluene, but readily soluble in chloroform and dichloromethane. Differential scanning calorimetry (DSC) of poly-6 shows the T_g to be 150°C . X-ray powder diffraction of poly-6 shows it to be almost entirely amorphous.

^1H NMR analysis of poly-6 shows that 1,6-polymerization has occurred, since the methyl resonance at 1.84 ppm in the monomer 6 has been replaced with a methyl resonance at 1.1 ppm in the polymer consistent with a vinylic methyl group in the monomer and a nonvinylic methyl group in the polymer. The absence of *cis* carbon-carbon double bonds in poly-6 is inferred from the absence of large (4–5 ppm) ^{13}C NMR chemical shift differences in the resonances of the methine and quaternary carbon α to the double bonds of poly-6. Such chemical shift differences for *cis* and *trans* dienes have been reported²¹ to be quite similar to those characteristic of *cis* and *trans* olefins.¹⁷ Irradiation of a solution of poly-6 with ultraviolet light in the presence of a catalytic amount of iodine resulted in no detectable change in the ^{13}C NMR spectrum of the polymer, providing additional evidence that the double bonds in poly-6 are *trans*. The ultraviolet absorption maximum of a chloroform solution of poly-6 at 251 nm (ϵ 17800) is more like that of cyclohexadiene (256.5 nm, ϵ 8000) than that of hexadiene (227 nm, ϵ 22500).²² However, the value of the extinction coefficient is clearly too high to be ascribed to a *cis* diene.²³ The ultraviolet spectroscopic data could be accommodated by a mixture of *cisoid* and *transoid* conformations of the *trans* double bonds.

The resolution enhanced 400-MHz ^1H NMR spectrum of poly-6 (Figure 4A) shows that the methyl resonance consists of a doublet and a triplet, the latter probably coming from two overlapping doublets. This was confirmed by a decoupling experiment in which the methine proton resonances, which appear as at least two complex patterns at about 2.65, were irradiated. The methyl resonances then collapsed to give three single lines,

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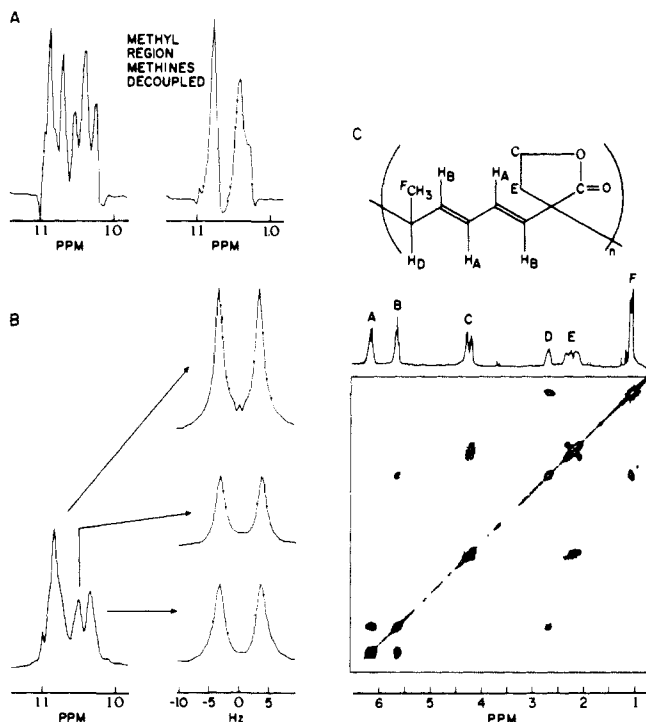


Figure 4. 400-MHz ^1H NMR spectra of poly-6. A: methyl region with resolution enhancement. B: 2D J -resolved, methyl region of projection on chemical shift axis showing decoupling. C: 2D-COSY spectrum.

two of them overlapping. Owing to the width of the methine resonances, it is difficult to decouple all of the methyl resonances simultaneously, and decoupling the methyl resonances is via the two-dimensional J -resolved NMR spectrum. The projection along the f_2 axis of this spectrum contains only chemical shift information, all couplings having been removed. The methyl region of the two-dimensional J -resolved NMR spectrum is shown in Figure 4B. There are three main peaks in roughly the ratios 2:1:1. The perpendicular slices of the two dimensional spectrum at the top of each peak contain the spin-spin coupling patterns, which are the expected 7-Hz doublets. The three methyl proton resonances may be accounted for if the chemical shifts for the methyl resonances are determined by erythro and threo diastereomeric centers in different conformational environments due, for instance, to transoid and cisoid arrangements of the double bonds, with an accidental degeneracy in one of the environments. To confirm the ^1H NMR assignments, a two-dimensional chemical shift correlated spectroscopy (COSY) experiment was carried out. The COSY spectrum is shown in Figure 4C. Off-diagonal elements indicate couplings between peaks lying along the diagonal and confirm the assignments shown.

The ^{13}C NMR spectrum shows two resonances each for the methine carbon and the methyl carbon (i and j, respectively, in Figure 5). The high-field set of resonances (41.8 and 14.3 ppm) is assigned to the erythro diastereotopic carbons (i and j in Figure 5), and the low-field set of resonances (42.3 and 15.5 ppm) is assigned to the threo diastereotopic carbons (i and j). Although this assignment appears to be inconsistent with the erythro-threo ^{13}C NMR assignments in the case of poly-4, if we examine the steric interactions in the two polymers as shown in Figure 6, it is apparent that the erythro polymer has more serious gauche interactions between the methyl group and the hydrogen atoms of the five-membered ring than the threo polymer has in the gauche interaction between the methyl group and the lactone group. Since the more hindered diastereomer is expected to resonate at higher field, we assign the high-field resonances to the erythro polymer. This is completely consistent with the assignments for poly-4, since poly-4 has a hydrogen atom at the α -diastereotopic carbon instead of a cyclic methylene group (as in poly-6). Thus, the only important gauche interactions are between the methyl and the ester in the threo junction (see Figure

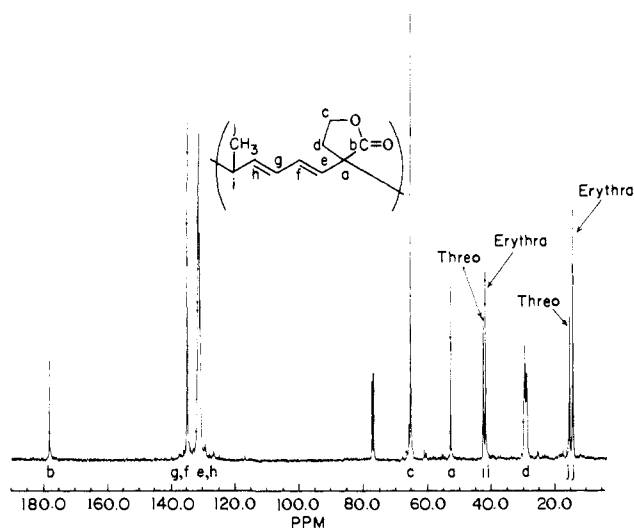


Figure 5. 100.6-MHz ^{13}C NMR spectrum of poly-6 (CDCl_3).

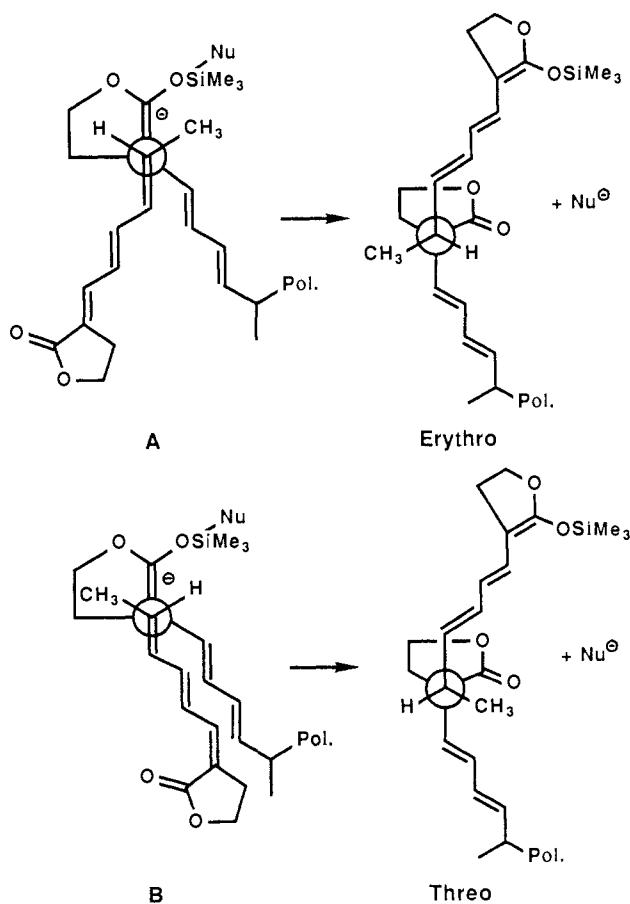


Figure 6. Antiperiplanar transition states leading to threo and erythro poly[3-(2,4-hexadien-1-ylidene)-4,5-dihydrofuranone] (poly-6).

2), and the high-field resonances in poly-4 are assigned to the threo polymer. The expected chemical shift differences between the diastereotopic carbons a and b (Figure 5) are, unfortunately, too small to permit integration or measurement of the individual chemical shifts.

It is of particular significance that integrations of the 42.3 and 41.8 ppm peaks show equal intensities as do the integrations of the 15.5 and 14.3 ppm peaks. Thus, ^{13}C NMR spectroscopy shows equal amounts of erythro and threo diastereomers, consistent with the results of the ^1H NMR experiments. The ^{13}C NMR results confirm that **6** undergoes GTP with no diastereoselectivity. This contrasts with the 2:1 erythro selectivity of **4** and the 2:1 meso selectivity observed with **5**. Examination of molecular models of

Table II. Initiation of Group Transfer Polymerization of MMA with Silyl Polyenoates and Related Compounds^a

entry	initiator, mmol	catalyst, μmol	\bar{M}_n (theory)	\bar{M}_n	\bar{M}_w	<i>P</i>
1	10 , 2	Bu ₄ N <i>m</i> CB, ^b 10	6100	7060	8310	1.18
2	10 , 2	Bu ₄ NBB, ^c 10	15 100	19 000	25 400	1.34
3	11 , 1	Bu ₄ NBB, 10	10 100	9760	14 300	1.46
4	12 , 4	Bu ₄ NBB, 30	1450	2170	2790	1.29
5	13 , 3.3	TASHF ₂ , 40	3100	3910	4570	1.17
6	14 , 2	Bu ₄ NBB, 10	15 150	20 100	28 800	1.43
7	14 , 1	Bu ₄ N <i>m</i> CB, 5	5125	5910	6630	1.12
8 ^d	16 , 1	TASHF ₂ , 10	5100	14 400	35 600	2.47
9 ^d	16 , 1	TASHF ₂ , 10	2100	8480	22 900	2.70

^a Polymerizations were carried out in THF solution, with feeding of monomer at a rate to maintain a temperature of 35–40 °C. Yields are 100% unless otherwise indicated. ^b Bu₄N*m*CB = tetrabutylammonium *m*-chlorobenzoate. ^c Bu₄NBB = tetrabutylammonium bibenzoate. ^d Batch, rather than feed, polymerization; catalyst added to solution of monomer and initiator.

the antiperiplanar transition states leading to erythro and threo diastereomers (Figure 6) suggests that transition state A has fewer nonbonded interactions than B. Another conformer of B, however, appears to be similar in energy to A since the interactions of the methyl group with the lactone ring hydrogen atoms are removed. Because the rates of erythro and threo diastereomer formation are similar, we conclude that antiperiplanar transition state A leads to formation of erythro diastereomeric units and that a rotational isomer of transition state B is responsible for formation of threo diastereomeric units. It is particularly interesting that the absence of diastereoselectivity in GTP of **6** closely parallels the small (1.2:1) 1,3-diastereoselection for *m* dyads (relative to *r* dyads) in GTP of 2-methylenebutyrolactone.^{1c}

Copolymerization with Acrylic Monomers. Since the initiation of GTP of most of the monomers in this study with silyl ketene acetals was inefficient, with \bar{M}_n generally much higher than theory, we might expect that group transfer copolymerization of polyunsaturated monomers, with, for example, methyl methacrylate would not be very favorable. In an experiment designed to prepare an AB block copolymer of MMA and **1**, living PMMA (\bar{M}_n 2950, \bar{M}_w 3950, *P* = 1.34) was prepared and then treated with **1**. Conversion of both the monomers was 100%. However, only a small portion of the PMMA initiated a poly-**1** block as confirmed by the gel permeation chromatogram, which was bimodal with about 30% of the polymer having \bar{M}_n 3220 (unreacted PMMA) and 70% having \bar{M}_n 24 700 (block copolymer of MMA and **1**). Thus, the rate of propagation of **1** is much faster than the rate of initiation of GTP of **1** by the living PMMA. We estimate that about 77% of the living PMMA failed to initiate polymerization of **1**. Addition of MMA or ethyl acrylate to the reaction mixture following polymerization of **1** failed to result in any further polymerization. Observation of a single *T_g* at 16.2 °C indicates a lack of phase separation in the mixture of PMMA and block copolymer.

In a competition experiment between MMA and **1**, a solution containing equimolar quantities of MMA and **1** and a catalytic amount of TASHF₂ was treated with **7** and was then quenched with methanol before polymerization was complete. ¹H NMR analysis showed that all of the methyl pentadienoate (**1**) had polymerized, and only about 10% of the MMA had polymerized. The molecular weight distribution of the resulting polymer was very broad (\bar{M}_n 12 700, \bar{M}_w 99 900, *P* = 7.8). In a batch copolymerization of MMA and **1** initiated with the silyl ketene acetal **8** and TASHF₂, two successive exotherms were observed, and the gel permeation chromatogram was bimodal with molecular weight maxima at 6310 and 31 600, which suggests that, for the most part, two homopolymers were formed. Thus, because of the great disparity in rates of polymerization between **1** and MMA, copolymers with controlled structure are not readily prepared.

When living poly-**2** was treated with MMA, 33% of the added MMA polymerized forming an AB block copolymer containing 79% poly-**2** and 21% PMMA. The GPC MW peak increased from 48 000 to 53 000 (theoretical increase, 3200). When GTP of MMA was carried out in the presence of 5 mol % **2**, conversion of the monomers was quantitative to produce polymer with \bar{M}_n 6560, *P* = 1.28, but a distinct low molecular weight tail in the

GPC trace suggests that random copolymerization did not occur. Similar results were obtained in copolymerization of 5 mol % ethyl sorbate with MMA. Initiation of GTP of **4**, with living PMMA (\bar{M}_n 6420, *P* = 1.28), however, produced a block copolymer with \bar{M}_n 17 600, *P* = 1.68 (theoretical \bar{M}_n 23 000). A modest low molecular weight tail in the GPC trace of the copolymer indicated that a small amount of the PMMA failed to initiate GTP of **4**. Thus, **4** performs somewhat better than other monomers in this study in forming block copolymers with MMA by initiation with living PMMA. The reason is believed to be the relatively slow propagation rate of **4** such that propagation and initiation by a polymeric silyl ketene acetal are comparable in rate.

Initiation of Polymerization of MMA with Silyl Polyenoates.

Initiation of GTP of MMA with silyl polyenoates was examined to determine whether efficient initiation with good control of molecular weight would obtain, and, more importantly, to determine the regiochemistry and stereochemistry of the Michael addition process. The silyl polyenoates **10–14** as well as the 4-(trimethylsilyl)-2-butenolate **16** were used successfully to initiate polymerization of MMA, and in some cases the control of molecular weight and polydispersity were excellent. The results are summarized in Table II. The 1,4-bis(trimethylsilyloxy)-1,3-butadiene (**15**), which had given poor control of molecular weight in initiation of **2** (see Table I, entry 7), gave poor conversions in initiation of MMA as well as ethyl acrylate.

Since the silyl dienolate **10** appears to initiate polymerization of polyenoates with a higher rate of initiation than that of the silyl ketene acetal **7**, we would expect that the higher reactivity of silyl polyenoates would result in initiation of GTP of MMA with a rate of initiation greater than the rate of propagation. This should produce good control of molecular weight and low polydispersity. It is apparent from the molecular weight data in Table II that there is reasonable agreement between theoretical \bar{M}_n and observed \bar{M}_n of PMMA prepared with the initiators **10** (entries 1 and 2), **11** (entry 3), **12** (entry 4), **13** (entry 5), and **14** (entries 6 and 7). PMMA with very low polydispersity was obtained with the initiators **10**, **13**, and **14**. The formation of PMMA with higher \bar{M}_n than theory and high polydispersity when the silyl ester **16** is the initiator is not surprising, since *C*-silyl compounds are often less reactive than *O*-silyl compounds. In this case, initiation is slower than propagation.

Regio- and Stereochemistry of Initiation of GTP of MMA. The Michael addition of **10** to MMA, which is the initiation step in GTP of MMA initiated by **10**, can, in theory, proceed by either of two routes. Reaction at the 2-position of the diene would lead to PMMA with an isolated terminal vinyl group as in **17** (Scheme X), while reaction at the 4-position would lead to PMMA with an ethyl crotonate terminal group as in **18** (Scheme X). An earlier study⁴ of the regiochemistry of the reaction of **10** with benzaldehyde showed that both possible regioisomers were formed with nearly exclusive 2-substitution at –95 °C and nearly exclusive 4-substitution at 34 °C. ¹H NMR analysis of the end group of low molecular weight PMMA prepared by initiation with **10** revealed the presence of three vinyl hydrogen atoms (5.5–5.7 ppm, 1 H; 4.95–5.1 ppm, 2 H) as well as the allylic hydrogen atom (mult, 2.85–3.1 ppm, 1 H) and the OCH₂ group (4.055, 2 H)

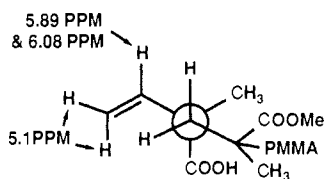
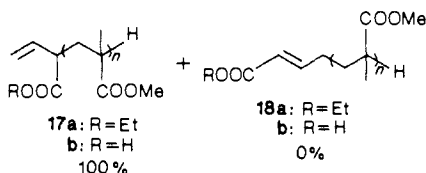
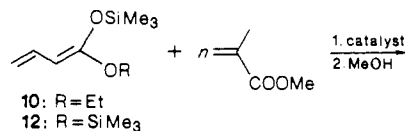
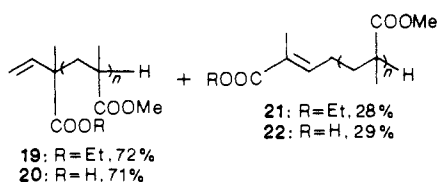
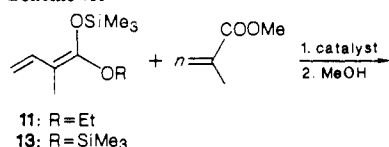


Figure 7. End group of one of the two regioisomers of PMMA prepared by initiation with **13**.

Scheme X



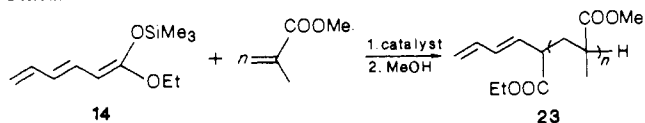
Scheme XI



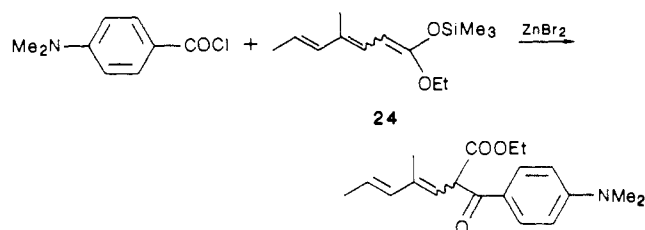
consistent with the structure, **17a** (Scheme X). There was no low-field resonance characteristic of structure **18a**. Thus, the aldehyde reaction model⁴ does not predict the correct regiochemistry for initiation of MMA by **10**. At a temperature at which the reaction of **10** with benzaldehyde produced almost exclusive 4-substitution, the Michael reaction with MMA gave only substitution at the 2-position. ¹H NMR analysis of the end group of PMMA prepared with the disilyl dienolate **12** as initiator (Table II, entry 4) showed that structure **17b** was formed to the exclusion of **18b**.

Initiation of GTP of MMA with **11** produced both possible regioisomeric end groups as indicated by ¹H NMR analysis (Scheme XI). The polymer **19** resulting from initiation at the 2-position of **11** comprised 72% of the product, while the remaining 28%, **21**, resulted from initiation at the 4-position. Initiation of GTP of MMA with the disilyl dienolate **13** gave 71% of the product, **20**, resulting from reaction at the 2-position and 29% of the product, **22**, resulting from reaction at the 4-position. The results with **11** and **13** are, within experimental error, identical. The formation of products of initiation at the 4-position of **11** and **13** and the absence of such products when the initiators are **10** or **12** is attributed to the steric hindrance due to the 2-methyl group of **11** and **13**. Further analysis of the end group of **20** was performed by using ¹H NMR decoupling experiments to obtain stereochemical information. Irradiation of the 5.1 ppm resonance of **20** (m, 2 H, C=CH₂) collapsed the multiplets at 5.89 and 6.08 ppm (total of 1 H), which shows that both multiplets are due to vinylic hydrogen atoms of a double bond joined to a diastereotopic carbon atom (Figure 7). The nonequivalence of the vinylic hydrogen atoms is due to the 1,3-threo and 1,3-erythro relation of the carbon derived from C-2 of the initiator and the chiral center of the first MMA unit. From the intensities of the resonances it is apparent that the two stereoisomers are present in unequal amounts—about 63% and 37%. Unfortunately, suitable models

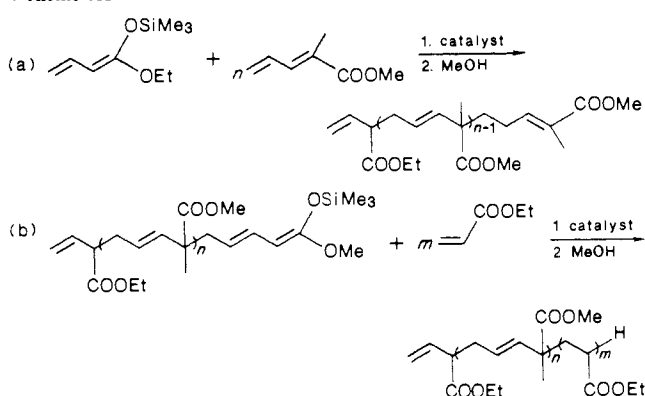
Scheme XII



Scheme XIII



Scheme XIV



are not available to permit us to determine which isomer is 1,3-threo and which is 1,3-erythro.

¹H NMR analysis of the end group of low molecular weight PMMA prepared with the silyl trienoate **14** as initiator showed clearly that initiation occurred only at the 2-position (Scheme XII). No resonances were detected in the 7 ppm region characteristic of a vinylic hydrogen on a double bond conjugated to an ester. Thus, the only product of initiation of GTP of MMA with the silyl trienoate **14** is PMMA with a terminal butadienyl group, **23**. Fleming, Iqbal, and Krebs²⁴ have reported that the silyl trienoate **24** underwent zinc bromide catalyzed reaction with *p*-(dimethylamino)benzoyl chloride at the 2-position (Scheme XIII). Thus, the enhanced reactivity toward electrophiles at the 2-position of silyl trienoates may be general. On the other hand, Ohno, Mori, and Eguchi have reported that 1-methoxy-1-(trimethylsilyloxy)-1,3,5-hexatriene undergoes reactions with dienophiles at the 3- and 6-positions.¹⁰

The regiochemistry of initiation of **2** with **10** was more difficult to determine by ¹H NMR analysis of the end group because of interference from the backbone double bonds and conjugated double bond formed by protonolysis of the living end (see Scheme XIVa). In order to prevent the formation of a conjugated double bond from the living end group, a block of ethyl acrylate was added to the living poly-**2** (Scheme XIVb). This permitted identification of a terminal C=CH₂ group, and the absence of any resonance attributable to a vinyl proton on a double bond conjugated to an ester group eliminated the possibility of an end group analogous to that of **18a**. Thus, we conclude that the regiochemistry of initiation of polymerization of a dienolic ester is the same as that of initiation of polymerization of MMA. The initiation occurs at the 2-position of **10**.

Mechanistic Implications. GTP of alkyl 2-methylpentadienoates has been shown to be faster than GTP of methacrylates, and, when the initiator is a silyl polyenoate, there is better control of molecular weight, and the polydispersity of the resulting polymers is lower than when the initiator is a silyl ketene acetal. Moreover,

(24) Fleming, I.; Iqbal, J.; Krebs, E.-P. *Tetrahedron* **1983**, *39*, 841.

living ends of the unquenched polymers show good retention of activity during a 1-h holding period. The high rate of polymerization in the diene system relative to the methacrylate system can be ascribed to the lower LUMO of the monomer and the higher HOMO of the silyl polyenolate end of the polymer in the diene system.²⁵ Studies to date on the mechanism of GTP of methacrylates have not been able to provide conclusive data on the timing of the C-C bond formation and the silicon transfer steps. Although, in GTP of MMA synchronous bond formation and silicon transfer by way of a cyclic (8-membered ring) transition state is a possible pathway, in GTP of the polyenoates of the present study, such a synchronous cyclic transition state seems unlikely for the transition states shown in Figure 2. It would be even less probable in the case of GTP of the triene lactone **6**. Instead, it seems likely that C-C bond formation precedes formation of a new Si-O bond at the carbonyl oxygen via an open transition state in which developing charges are delocalized over several atoms. Indeed, dissociation of the silicon may even precede carbon-carbon bond formation, with resilylation preceding further reaction with monomer. Such a dissociative process has been proposed for the anion-catalyzed reaction of **10** with benzaldehyde.⁴ To determine the intramolecularity of the silicon transfer in GTP of polyenoates, double labeling experiments would be required, similar to those reported for GTP of MMA.²⁶

Although direct bond formation between C-2 of the silyl polyenolate end group and C-5 of the monomer is the simplest mechanism for the propagation step, the observed product would also be accounted for by initial formation of a bond between C-4 of the silyl polyenolate end group and C-3 of the monomer followed by a Cope rearrangement as shown in Scheme XV. In fact, Ballester and co-workers²⁷ have very elegantly demonstrated just such a sigmatropic rearrangement in the Michael addition of the lithium dienolate derived from 2-butenic acid to 1,3-diphenylpropenone, which occurs through a 1,2-addition followed by a sigmatropic rearrangement. At -95 °C the 1,2-adduct was stable to rearrangement. We found that GTP of **2** with **10** and TASHF₂ catalyst at -75 °C (Table I, entry 8) or with **10** and acetate catalyst at -95 °C gave normal poly-**2** in quantitative yield. This is suggestive that a Cope rearrangement is not involved in this system, since the sequential sigmatropic rearrangements would be expected to be too slow at these low temperatures to produce polymer.

The effects of substituents on GTP of polyenoates is important. A substituent in the 2-position enhances the livingness of the polymer as exemplified by the livingness experiment with poly-**2**. A methyl group at the 5-position of ethyl sorbate retards the rate of polymerization to such an extent that it is competitive with that of GTP of MMA, and living PMMA prepared by GTP can be used to initiate polymerization of **4** with formation of an AB block copolymer in which there is reasonably good control of the B block molecular weight. In contrast, living PMMA initiates monomers such as **2** too slowly relative to the propagation rate of **2** to be able to control the size of the B block. Unlike the 5-methyl group of **4** the ω-methyl group of the triene lactone **6** does not retard the rate of propagation sufficiently to permit controlled initiation by a silyl ketene acetal, and high molecular weight polymer is formed even with stoichiometric **7**. This may be due to reduced steric hindrance in a system with six carbon atoms per repeat unit compared to the four carbon atom repeat unit of **4**. Or it may be due to a greater complexation of catalyst in the longer conjugated systems.

Conclusions

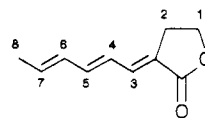
GTP has been extended to polyunsaturated monomers. The structure of the polymeric triene lactone poly-**6** prepared by GTP has been shown to be completely random with respect to diast-

ereoselection. The 2:1 diastereoselectivity found in GTP of **4** and **5**, leading to excess of the less hindered polymers, is consistent with antiperiplanar transition states. The demonstration of sequential Michael additions of polyunsaturated esters provides a facile route to acyclic structures containing multiple double bonds, which are potential sites for further synthetic elaboration. The silyl polyenolates **10**, **12**, and **14** have been shown to provide rapid initiation of GTP of MMA as well as polyenoates. The regio-specific initiation at the 2-position provides a methodology for preparation of acrylic polymers having exactly one vinyl or butadienyl end group. This regioselectivity contrasts with the temperature-controlled regioselectivity of **10** in the reaction with benzaldehyde.⁴ The presence of a 2-methyl group in **11** and **13** results in loss of regioselectivity in initiation of GTP of MMA.

Experimental Section

Materials and Methods. An earlier publication^{1c} provides details for purification of solvents and monomers as well as procedures for carrying out the polymerizations. The same gel permeation chromatographic equipment and standards (PMMA) were used. The values of M_w/M_n are reported as *P*. Methyl pentadienoate was purchased from Fluka, redistilled, and passed over a column of neutral alumina under argon. Ethyl sorbate was purchased from Aldrich Chemical Co. and passed over a column of neutral alumina under argon. Methyl sorbate was purchased from Frinton Laboratories, distilled, and passed over a column of neutral alumina under argon. Ethyl muconate was prepared by the sulfuric acid catalyzed reaction of muconic acid with excess ethanol, followed by recrystallization from *n*-heptane. Ethyl and methyl 2-methylpentadienoate⁷ were purified by distillation and passage through a column of neutral alumina under argon. The silyl ketene acetals and silyl polyenolates were prepared as described earlier.^{1c,4,6} Tetrabutylammonium acetate, bibenzoate, and *m*-chlorobenzoate were prepared and purified as described earlier.²

(E,E,E)-3-(2,4-Hexadien-1-ylidene)-4,5-dihydro-3(3H)-furanone (6). In a reaction flask fitted with a mechanical stirrer was placed 5.05 g (0.126 mol) of 60% sodium hydride dispersion in mineral oil. After this was washed three times with toluene to remove the mineral oil, 330 mL of toluene and 28 g (0.126 mol) of 2-(diethylphosphono)-4-butyrolactone⁸ were added. When the addition was complete, the mixture was stirred at 50–60 °C until hydrogen evolution had ceased (about 30 min). After cooling to 20 °C, 12.12 g (13.9 mL, 0.126 mol) of sorbaldehyde was added. After stirring at 80 °C for 2 h, the mixture was filtered hot, and the filtrate was evaporated under reduced pressure to 18 g of oil, which gradually crystallized. Recrystallization from carbon tetrachloride-heptane and from toluene-heptane gave 2.5 g of pale yellow crystals, mp 94–99 °C. Sublimation at 85–90 °C (0.1 mm) gave colorless crystals of **6**, mp 99.5–100.5 °C. Anal. Calcd for C₁₀H₁₂O₂: C, 73.15; H, 7.37; *m/z* 164.0837. Found: C, 71.31; H, 7.21; *m/z* 164.0836. GC showed a purity of 99.44%. UV (CHCl₃): 315 nm (ε 39 100). IR (CHCl₃): 1745 (C=O), 1650, 1625 cm⁻¹ (C=C). ¹H NMR (CDCl₃, 360 MHz, *J* in hertz): δ 1.84 (d, *J* = 6, 3 H, Me-8), 2.98 (td, *J* = 7, ⁴*J* = 3, 2 H, CH₂-2), 4.40 (t, *J* = 7, 2 H, OCH₂-1), 5.99 (dq, *J*_{tr} = 15, *J*_{Me} = 6, vinyl H-7), 6.1–6.3 (m, 2 H, vinyl H-5 and H-6), 6.57 (dd, *J*_{H5} = 15, *J*_{H3} = 12, 1 H, vinyl H-4), 7.1 (dt, *J*_{H4} = 12, ⁴*J* = 3, 1 H, vinyl H-3).



1,1-Bis(trimethylsiloxy)-2-methyl-1,3-butadiene (13). To a solution of 42 mL (0.3 mol) of diisopropylamine in 500 mL of tetrahydrofuran at 0 °C was added 0.3 mol of *n*-butyllithium (1.6 M in hexane). After 30 min at 0 °C, the solution was cooled to -78 °C, and a solution of 14 g (0.14 mol) of tiglic acid in 50 mL of tetrahydrofuran was added at -78 °C. After 1 h at -78 °C, 38 mL (0.3 mol) of chlorotrimethylsilane was added at -78 °C. After slowly being warmed to room temperature, the solution was evaporated. The residue was treated with dry hexane and filtered under argon, the filtrate was evaporated, and the residue was distilled twice in a small spinning-band column to give 5.4 g of 1,1-bis(trimethylsiloxy)-2-methyl-1,3-butadiene (**13**), bp 38 °C (0.5–0.2 Torr), density 0.86. ¹H NMR (360 MHz, CDCl₃, *J* in hertz): δ 0.22 (2 s, 18 H, OSiMe), 1.62 (s, 3 H, C=Me), 4.71 (dd, *J* = 10, 2, 1 H, C=CH), 4.77 (dd, *J* = 18, 2, 1 H, C=CH), 6.66 (dd, *J* = 18, 10, 1 H, C=CH). Anal. Calcd for C₁₁H₂₄O₂Si₂: C, 54.04; H, 9.90; Si, 22.98; *m/z* 244.1315. Found: C, 54.11; H, 9.79; Si, 21.73; *m/z* 244.1310. GC shows 96% purity.

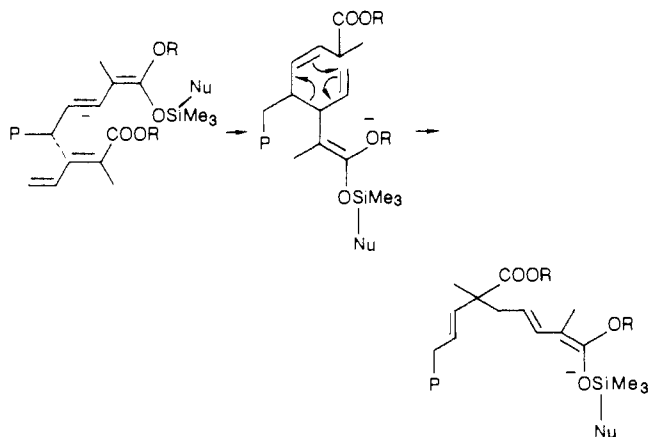
1,4-Dimethoxy-1,4-bis(trimethylsiloxy)-1,3-butadiene (15). The general procedure of Long and Rathke¹¹ for the ethyl analogue of **15**, with

(25) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976; p 114.

(26) Sogah, D. Y.; Farnham, W. B. *Organosilicon and Bioorganosilicon Chemistry: Structures, Bonding, Reactivity and Synthetic Application*; Sakurai, H., Ed.; Wiley: New York, 1985; Chapter 20.

(27) Ballester, P.; Garcia-Raso, A.; Gomez-Solivellas, A.; Mestres, R. *Tetrahedron Lett.* **1985**, 26, 2485.

Scheme XV



use of methyl succinate, gave 1,4-dimethoxy-1,4-bis(trimethylsilyloxy)-1,3-butadiene (**15**), bp 71–73 °C (0.2 Torr). $^1\text{H NMR}$ (360 MHz, CDCl_3 , J in hertz): δ 54.5% *Z,Z*; 27.3% *E,Z*; 18.2% *E,E* isomers: [0.21 (s, *Z,Z* SiMe), 0.23 (s, *E,E* SiMe), 0.19, 0.24 (2 s, *E,Z* SiMe) total 18 H], [3.53 (s, *Z,Z* OMe), 3.52 (s, *E,E* OMe), 3.54 (s, *E,Z* OMe) total 6 H], [4.37 (s, *Z,Z* C=CH), 4.53 (s, *E,E* C=CH), 4.40 (d, $J = 10$, *Z* C=CH of *E,Z*), 4.50 (d, $J = 10$, *E* C=CH of *E,Z*) total 2 H]. UV (MeCN): 240 nm (ϵ 4067), (isooctane) 243 nm (ϵ 11 852), (THF) 248 nm (ϵ 14 000). IR (neat): 1630 cm^{-1} (C=C). MS, m/z : observed 290.1372, calcd for $\text{C}_{12}\text{H}_{20}\text{O}_4\text{Si}_2$ 290.1369.

Polymerization of Methyl Pentadienoate (1). Methyl pentadienoate was distilled and then passed over a short column of neutral alumina under argon. To a stirred solution under an argon atmosphere of 2.9 mL (25 mmol) of methyl pentadienoate and 100 μL of tetrabutylammonium acetate² (0.01 M in THF) in 10 mL of THF at 0 °C was added 0.1 mL (0.5 mmol) of 1-methoxy-1-(trimethylsilyloxy)-2-methyl-1-propene (**7**). The solution was allowed to warm to 13 °C whereupon a pale yellow color appeared, the temperature of the solution rapidly rose to 45 °C, and the solution became viscous. A sample of the reaction mixture was removed for analysis. $^1\text{H NMR}$ spectroscopy showed that there was no residual monomer in the solution. GPC showed \bar{M}_n 37 000, \bar{M}_w 123 000, $P = 3.33$ (theory, \bar{M}_n 5700). The tacky polymer was precipitated in hexane, dissolved in dichloromethane, washed with water and brine, dried (MgSO_4), and evaporated to 2.3 g of tacky poly(methyl pentadienoate), poly-1. Differential scanning calorimetry (DSC) shows a T_g at 1.6 °C. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 2.17 (m, 1 H, CH_2), 2.35 (m, 1 H, CH_2), 2.96 (m, 1 H, CH), 3.60 (2s, 3 H, OMe), 5.41 (m, 2 H, C=CH). $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3): δ 35.31 (s, CH_2), 48.75 (s, CH), 51.49 (s, OMe), 129.43 (s, C=C), 173.51 (s, C=O).

General Procedure for Polymerization of Polyenoates by Monomer-Feed Process. Polymerization of Methyl 2-Methylpentadienoate (2). To a stirred solution of 0.22 mL (1 mmol) of (90% *Z*) 1-ethoxy-1-(trimethylsilyloxy)-1,3-butadiene⁴ (**10**) and 50 μL of tetrabutylammonium *m*-chlorobenzoate² (0.1 M in THF) in 30 mL of THF under an argon atmosphere was added dropwise 4 mL (30 mmol) of methyl 2-methylpentadienoate⁷ (purified by passage over a short column of neutral alumina under argon) at a rate such that the temperature did not exceed 35 °C. A small sample was removed for analysis. $^1\text{H NMR}$ analysis showed no residual monomer. GPC: \bar{M}_n 8440, \bar{M}_w 9950, $P = 1.18$ (theory, \bar{M}_n 3900). After 1 h, an additional 4 mL (30 mmol) of methyl 2-methylpentadienoate was added at a rate such that the temperature did not exceed 35 °C. Analysis of a sample of the solution by $^1\text{H NMR}$ spectroscopy showed no residual monomer. GPC: \bar{M}_n 11 800, \bar{M}_w 16 000, $P = 1.35$ (theory, \bar{M}_n 7700). After addition of 1 mL of methanol, the solution was evaporated to give 7.4 g of liquid poly-2. \bar{M}_n as determined by vapor phase osmometry (VPO) in toluene was 10 400.

General Procedure for Batch Polymerization of Polyenoates. Polymerization of Methyl 2-Methylpentadienoate (2). To a stirred solution of 6.6 mL (50 mmol) of methyl 2-methylpentadienoate (purified over a short column of neutral alumina under argon) and 10 μL of TASHF₂ (0.1 M in acetonitrile) in 50 mL of THF in an argon atmosphere was added 55 μL (0.25 mmol) of **10**. The temperature of the solution rapidly rose 17 °C (to 42.4 °C). A sample of the reaction mixture was removed for analysis. $^1\text{H NMR}$ analysis showed no residual monomer. GPC: \bar{M}_n 46 500, \bar{M}_w 58 700, $P = 1.26$ (theory, \bar{M}_n 25 200). After addition of 1 mL of methanol, the polymer was precipitated with hexane as a gum, dissolved in dichloromethane, washed with brine, dried (MgSO_4), and evaporated to 5.2 g of gummy poly(methyl 2-methylpentadienoate). VPO in toluene, \bar{M}_n 35 000. DSC: T_g 2.8 °C. Intrinsic viscosity in CHCl_3 , 0.461. $^1\text{H NMR}$ (300 MHz, CDCl_3 , J in hertz): δ 1.16 (s, 3

H, CMe), 2.18 (m, 1 H, CH_2), 2.44 (m, $J = 7$, 1 H, CH_2), 3.62 (s, 3 H, OMe), 5.34 (m, $J_{\text{H}_2} = 17$, 1 H, vinyl H-3), 5.62 (d, $J_{\text{H}_3} = 17$, 1 H, vinyl H-2).

Polymerization of Ethyl 2-Methylpentadienoate (3). Batch polymerization of 4 g (4.35 mmol) of ethyl 2-methylpentadienoate with 0.05 mL (0.25 mmol) of **7** and 10 μL of TASHF₂ (1.0 M in acetonitrile) gave 3.5 g of poly(ethyl 2-methylpentadienoate) as a gum. GPC: \bar{M}_n 52 600, \bar{M}_w 228 000, $P = 4.33$ (theory, \bar{M}_n 20 000). DSC: T_g -27 °C. IR (film): 3040 (=CH), 1730 cm^{-1} (unconjugated ester C=O), 975 cm^{-1} (trans C=C). $[\eta]^{\text{chf.25}}$ 0.9605. $^1\text{H NMR}$ (360 MHz, CDCl_3 , J in hertz): δ 1.17 (s, 3 H, α -Me), 1.24 (t, $J = 7$, 3 H, Me of Et), 2.18, 2.46 (2 m, $^2J = 14$, $^3J = 7$, 2 H, chain CH_2), 4.10 (q, $J = 7$, 2 H, OCH₂), 5.02 (d, $J = 16$, 1 H, CCH=), 5.36 (dt, $J = 7$, 16, 1 H, $\text{CH}_2\text{CH}=\text{C}$). $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3): δ 14.09 (α -Me), 20.82 (Me of Et), 42.37 (chain CH_2), 48.20 (quaternary C), 60.45 (OCH₂), 124.64 ($\text{CH}_2\text{C}=\text{C}$), 137.05 (CCH=), 174.99 (C=O).

Polymerization of Ethyl Sorbate (4). Batch polymerization of 7 g (50 mmol) of ethyl sorbate with 0.1 mL (0.5 mmol) of **7** and 60 μL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF) produced a temperature increase from 25 to 35 °C during a period of 30 min. A sample was removed for analysis. $^1\text{H NMR}$ analysis showed no residual monomer. GPC: \bar{M}_n 18 700, \bar{M}_w 36 800, $P = 1.97$ (theory, \bar{M}_n 14 100). After 1 h, 3.5 g (25 mmol) of ethyl sorbate was added which produced a slow temperature rise of 2 °C. $^1\text{H NMR}$ analysis of a sample showed that 35% of the second charge of monomer had polymerized. After repeated precipitations there was obtained 4 g of tacky poly(ethyl sorbate). GPC: \bar{M}_n 29 800, \bar{M}_w 58 800, $P = 1.97$. \bar{M}_n (VPO in toluene at 50 °C): 24 500. $[\eta]^{\text{chf.25}}$ 0.376. DSC: T_g 6.6 °C. IR (CHCl_3): 1725 (ester C=O), 975 cm^{-1} (trans C=C). $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3): δ 173.0 (s, C=O), 136.3 (m, =C), 126.3 (m, =C), 60.1 (s, OCH₂), 55.5 (m, trans ω -CH), 50.1 (m, cis ω -CH), 39.6 (m, trans α -CH), 34.5 (m, cis α -CH), 18.3 (m, ω -Me), 14.0 (s, ester Me). $^1\text{H NMR}$ (360 MHz, CDCl_3): δ 0.9 (m, 3 H, CH_3CH), 1.21 (m, 3 H, CH_3CH_2), 2.42, 2.7 (2 m, 2 H, CH, CH), 4.04 (m, 2 H, OCH₂), 5.36 (m, 2 H $\text{CH}=\text{CH}$).

Reduction of Poly(ethyl sorbate) with Diimide. A mixture of 1 g (7.34 mequiv) of poly-4 (\bar{M}_n 43 000), 6.9 g (36.7 mmol) of *p*-toluenesulfonhydrazide, and 20 mL of diethylene glycol dimethyl ether was stirred at 140 °C for 12 h under argon. The mixture was poured into 50% aqueous methanol, and the gummy precipitate was extracted four times with 50-mL portions of methanol. The residue was dissolved in dichloromethane and precipitated in hexane to give 0.66 g of poly-4H as a gum. GPC: \bar{M}_n 62 800, \bar{M}_w 118 000, $P = 1.89$. DSC: T_g -9.8 °C. $^1\text{H NMR}$ (360 MHz, CDCl_3) shows broad, poorly resolved peaks, and a weak resonance at 5.4 ppm indicates that 8% of the original C=C remains unreduced. $^{13}\text{C NMR}$ (75.6 MHz, CDCl_3 , carbons numbered from C=O = 1): δ 14.35 (CH_3CH_2), 16.62 (erythro CH_3CH), 16.40 (threo CH_3CH), 26.19 (erythro CH_2 -3), 27.32 (threo CH_2 -3), 32.74 (CH_2 -4), 35.48 (CH-5), 51.88 (erythro CH-2), 51.04 (threo CH-2), 59.87 (OCH₂-2), 175.34 (erythro C=O), 175.00 (threo C=O). The intensity ratios of erythro:threo resonances are all approximately 2:1.

Polymerization of Methyl Sorbate. By use of the procedure for batch polymerization of **4** with initiation by **10** and catalysis by tetrabutylammonium acetate, 40% poly(methyl sorbate) was obtained as a solid polymer. DSC: T_g 33 °C. GPC: \bar{M}_n 6410, \bar{M}_w 8200, $P = 1.28$ (theory for 40% conversion, \bar{M}_n 5040). IR (KBr, ν cm^{-1}): 1735 (C=O), 1640 (vw, cis C=C), 970 (trans C=C). $^1\text{H NMR}$ (300.65 MHz, $\text{THF}-d_6$): δ 0.95 (br s, CH_3), 2.3–2.9 (m, CH), 3.53, 3.59, 3.62, 3.64 (OCH₃), 5.4 (s, =CH). $^{13}\text{C NMR}$ (75.6 MHz, CDCl_3): δ 173.44 (C=O), 137.94 (=C), 127.67 (=C), 56.46, 55.71 (trans $\text{CHC}=\text{O}$), 50.97, 50.43 (cis $\text{CHC}=\text{O}$), 51.58, 51.42 (OCH₃), 40.54, 40.34 (trans CHCH_3), 35.48 (cis CHCH_3), 18.34 (CH_3). The intensity ratio of trans:cis methine resonances is 3.5:1.

Reduction of Poly(methyl sorbate) with Diimide. The procedure used for reduction of poly-4 gave hydrogenated poly(methyl sorbate) as a gum. $^1\text{H NMR}$ shows 10% residual C=C. $^{13}\text{C NMR}$ (75.6 MHz, CDCl_3 , carbons numbered from C=O = 1): δ 16.58 (erythro CHCH_3), 16.32 (threo CHCH_3), 25.90 (erythro CH_2 -3), 27.10 (threo CH_2 -3), 32.30 (erythro CH_2 -4), 32.10 (threo CH_2 -4), 35.30 (CH-5), 51.25 (erythro OCH₃), 51.00 (threo OCH₃), 51.61 (erythro CH-2), 51.30 (threo CH-2), 175.80 (erythro C=O), 175.43 (threo C=O). Intensity ratio of erythro:threo resonances is about 2:1.

Polymerization of Ethyl Muconate (5). Batch polymerization of 7 g (35.3 mmol) of ethyl muconate with 100 μL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF) and 60- μL (0.25-mmol) portions (five required) of **10** until a slow exothermic reaction was observed produced a 10 °C increase in temperature. A sample was removed for analysis. $^1\text{H NMR}$ showed no residual monomer. GPC: \bar{M}_n 14 000, \bar{M}_w 33 500, $P = 2.39$. After addition of 1 mL of methanol, the solution was evaporated under reduced pressure, and the residue was precipitated twice from dichloromethane with hexane, dissolved in dichloromethane, washed with

water, dried (MgSO_4), and evaporated to 4.8 g of liquid poly-5. GPC: \bar{M}_n 16 900, \bar{M}_w 35 700, $P = 2.11$. IR (CHCl_3): 1732 (ester $\text{C}=\text{O}$), 970 cm^{-1} (trans $\text{C}=\text{C}$). $[\eta]$ 0.2381 (CHCl_3 , 25 °C). DSC: T_g 15.3 °C. ^1H NMR (360 MHz, CDCl_3): δ 1.145 (m, Me), 2.92–3.85 (br m's, CH), 4.02 (m, OCH_2), 5.05–5.65 (br m's, $=\text{CH}$). ^{13}C NMR (100.6 MHz, CDCl_3): δ 13.97 (s, Me), 46.10 (m, cis CH), 50.94 (m, trans CH), 60.87 (s, OCH_2), 128.88 (m, $=\text{CH}$), 170.88 (m, $\text{C}=\text{O}$). Intensity ratio of trans:cis methine resonances is 3:1.

Reduction of Poly-5 with Diimide. The procedure for diimide reduction of poly-4 was modified by extracting the crude polymer with 90% aqueous methanol because of the solubility of poly-5H in methanol. This gave poly-5H as a gum. ^1H NMR (360 MHz, CDCl_3): δ 1.19 (br s, CH_3), 1.42 (br, CH_2), 2.2–2.7 (br m's, CH), 4.05 (br s, OCH_2), 5.36, 5.50 (w br s, $=\text{CH}$). Integration of the ^1H NMR spectrum shows that there is 12% residual $\text{C}=\text{C}$. ^{13}C NMR (75.6 MHz, CDCl_3): δ 14.15 (CH_3), 26.66 (*dl* CH_2), 28.06 (meso CH_2), 46.63 (*dl* CH), 47.88 (meso CH), 60.55 (OCH_2), 173.13, 173.24 ($\text{C}=\text{O}$). The intensity ratio of meso:*dl* resonances is about 2:1.

Polymerization of 3-(2,4-Hexadien-1-ylidene)-4,5-dihydrofuranone (6). Batch polymerization of 0.82 g (5 mmol) of **6** with 1.0 mL (5 mmol) of **7** and 140 μL of tetrabutylammonium acetate (0.1 M in THF) resulted in a slow temperature rise of 2 °C accompanied by formation of an amber color and precipitation of polymer. Analysis of the supernate by ^1H NMR showed no residual monomer. The precipitated polymer was collected by filtration and washed with THF to give 0.48 g of colorless poly-6 as THF solvate. Evaporation of the filtrate gave 0.58 g of brown poly-6 as THF solvate. GPC of "THF-insoluble" poly-6 (from which part of the sample had to be removed by filtration in order to prepare the 0.25% solution in THF for GPC): \bar{M}_n 7240, \bar{M}_w 10900, $P = 1.51$. The polymer is readily soluble in dichloromethane, chloroform, and 1,2-dichloroethane but relatively insoluble in THF and toluene. The polymer tenaciously retained THF, which could be removed only after 2 days at 50–70 °C (0.1 Torr). The poly-6 retained the trimethylsilyl group, as evidenced by the ^1H NMR spectrum, which permitted the calculation of \bar{M}_n (10 000). ^1H NMR (360 MHz, CDCl_3): δ 0.14 (s, 0.013 H, SiMe), 1.05 (m, 3 H, Me), 2.2 (m, 2 H, CCH_2), 2.65 (m, 1 H, CH), 4.15, 4.24 (2m, 2 H, OCH_2), 5.6 (m, 2 H, $\text{C}=\text{CH}$), 6.1 (m, 2 H, $\text{C}=\text{CH}$). ^{13}C NMR (100.6 MHz, CDCl_3): δ 14.3 (m, erythro Me), 15.5 (m, threo Me), 29.1 (m, CCH_2), 41.8 (m, erythro CH), 42.3 (m, threo CH), 52.7 (m, quaternary C), 65.3 (s, OCH_2), 131.1 (m, $\text{C}=\text{CH}$, 2,5), 134.9 (s, $\text{C}=\text{CH}$, 3,4), 178.0 (m, $\text{C}=\text{O}$). A spin-echo experiment with gated decoupling supports the assignments for the resonances at 41.8, 15.5, 131.1, and 134.9 ppm since these resonances correspond to carbon atoms with an odd number of attached hydrogen atoms. UV (CHCl_3): 251 nm (ϵ 17 800). DSC: T_g 150.2 °C. TGA shows the onset of rapid weight loss at 370 °C. GPC of the "THF-soluble" poly-6: \bar{M}_n 1850, \bar{M}_w 9350, $P = 5$.

General Procedure for Preparation of Block Copolymers. Poly(methyl methacrylate-*b*-methyl pentadienoate). To a solution of 1.62 mL (15 mmol) of MMA and 20 μL of TASHF₂ (0.1 M in acetonitrile) in 30 mL of THF was added 0.1 mL (0.5 mmol) of **7**. The temperature rose from 25 to 33 °C. When the temperature had dropped to 28 °C, a sample was removed for analysis. ^1H NMR spectroscopy showed no residual monomer. GPC: \bar{M}_n 2950, \bar{M}_w 3950, $P = 1.34$. Then, 2.9 mL (25 mmol) of methyl pentadienoate (**1**) was added, and the temperature rapidly increased from 28 to 38 °C. A sample was removed for analysis. ^1H NMR showed no residual monomer. GPC: bimodal, 30% had \bar{M}_n 3220, \bar{M}_w 4250, $P = 1.32$; 70% had \bar{M}_n 24 700, \bar{M}_w 31 300, $P = 1.27$. Addition of 0.22 mL (2 mmol) of ethyl acrylate and 1.62 mL (15 mmol) of MMA caused no further increase in temperature. ^1H NMR analysis showed residual MMA. The polymer was precipitated as a gum in hexane, dissolved in dichloromethane, washed with water, dried (MgSO_4), and isolated as a gum. Comparison of the resonance intensities at 3.575 ppm (MMA OMe) and 3.63 ppm (poly-1 OMe) in the ^1H NMR spectrum (360 MHz, CDCl_3) of the product indicated 39 mol % PMMA and 61 mol % poly-1. DSC: T_g 16.2 °C.

Competitive Copolymerization of MMA and Methyl Pentadienoate. To a solution of 2.7 mL (25 mmol) of MMA, 2.9 mL (25 mmol) of methyl pentadienoate (**1**), and 10 μL of TASHF₂ (1.0 M in acetonitrile) in 20 mL of THF was added rapidly 0.2 mL (1 mmol) of **7**. A rapid temperature increase from 25 to 50 °C was interrupted with the addition of 0.5 mL of methanol to quench; a sample was removed for analysis. ^1H NMR analysis showed that about 10% of the MMA had polymerized and that all of **1** had polymerized. GPC: \bar{M}_n 12 700, \bar{M}_w 99 900, $P = 7.8$. The polymer was isolated by the general procedure of the previous experiment to give 1.8 g of gum. ^1H NMR spectroscopy shows the polymer consists of 88% poly-1 and 12% PMMA.

Poly(methyl 2-methylpentadienoate-*b*-methyl methacrylate). To a stirred solution of 0.11 mL (0.5 mmol) of **10** and 10 μL of TASHF₂ (0.1 M in acetonitrile) in 30 mL of THF was added 6.6 mL (50 mmol) of **2**

at a rate such that the temperature remained at 35 °C. A small sample was removed for analysis. ^1H NMR spectroscopy showed no residual monomer. GPC: \bar{M}_n 32 000, \bar{M}_w 46 000, \bar{M}_p 46 000, $P = 1.44$ (theory, \bar{M}_n 12 700). Then 5.4 mL (50 mmol) of MMA was added. The polymer was precipitated with hexane, dissolved in dichloromethane, washed with brine, dried (MgSO_4), and evaporated to 7.7 g of gummy polymer. ^1H NMR showed 79% poly-2 and 21% PMMA. DSC: T_g 5.8 °C. GPC: \bar{M}_n 27 800, \bar{M}_w 49 600, \bar{M}_p 53 000, $P = 1.78$ (theory, \bar{M}_n 22 700), \bar{M}_n 24 000 (VPO in toluene at 50 °C).

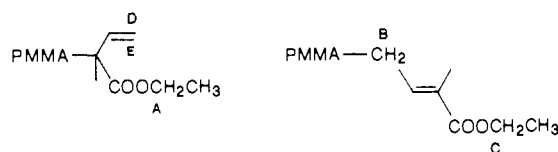
General Procedure for Random Copolymerizations. Random Copolymerization of Methyl 2-Methylpentadienoate and MMA. To a solution of 0.4 mL (2 mmol) of **7** and 0.1 mL of tetrabutylammonium bizenzoate (0.1 M in THF) in 40 mL of THF was added a mixture of 10.3 mL (95 mmol) of MMA and 0.66 mL (5 mmol) of **2** at a rate such that the temperature remained near 35 °C. When the exothermic reaction was over, 1 mL of methanol was added. A small sample was removed for analysis. ^1H NMR spectral data showed no residual monomers. GPC: \bar{M}_n 4790, \bar{M}_w 7300, $P = 1.52$ (theory, \bar{M}_n 5100). The polymer was precipitated with hexane, dissolved in THF, and precipitated with 1:1 methanol/water to give 9.8 g of copolymer, \bar{M}_n 6560, \bar{M}_w 8380, $P = 1.28$ (distinct low molecular weight tail in the GPC trace). ^1H NMR showed the composition to be 5% poly-2, 95% PMMA.

Random Copolymerization of Ethyl Sorbate and MMA. By use of the general procedure for random copolymerization, 5 mmol of ethyl sorbate (**4**) and 95 mmol of MMA were copolymerized with quantitative conversion to polymer with \bar{M}_n 4470, \bar{M}_w 6620, $P = 1.48$ (theory, \bar{M}_n 5100).

Poly(methyl methacrylate-*b*-ethyl sorbate). To a solution of 90 μL (0.43 mmol) of **7** and 10 μL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF) in 10 mL of THF was added 3.2 mL (30 mmol) of MMA. A sample was removed for analysis. GPC: \bar{M}_n 6420, \bar{M}_w 8230, $P = 1.28$ (theory, \bar{M}_n 7000). Then 30 μL of catalyst solution was added followed by 7.3 mL (50 mmol) of ethyl sorbate. The temperature slowly rose from 25 to 46 °C. A sample was removed for analysis. GPC: \bar{M}_n 17 600, \bar{M}_w 29 400, $P = 1.68$ (theory, \bar{M}_n 23 000). Addition of 3.2 mL of MMA and 30 μL of catalyst solution gave almost no thermal evidence of further polymerization. Precipitation with hexane twice gave 9.5 g of polymer. GPC: \bar{M}_n 19 600, \bar{M}_w 33 400, $P = 1.71$. Inherent viscosity 0.3 (CHCl_3 , 25 °C). DSC: T_g 18 °C. ^1H NMR shows the composition to be 52% poly-4, 48% PMMA.

General Procedure for Initiation of MMA Polymerization with Silyl Polylenolates. Initiation of Polymerization of MMA with 10. To a solution of 0.44 mL (2 mmol) of **10** and 0.1 mL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF) in 30 mL of THF was added 13 mL (120 mmol) of MMA. During 30 min, a slow increase of the temperature from 25 to 35 °C occurred. Addition of 0.1 mL of catalyst solution produced an increase in temperature to 41 °C. When the temperature had returned to 25 °C, 1 mL of methanol was added, and a sample was removed for analysis. ^1H NMR data showed no residual monomer. GPC: \bar{M}_n 7060, \bar{M}_w 8310, $P = 1.18$ (theory, \bar{M}_n 6100). Precipitation with 50% aqueous methanol gave 12.45 g of PMMA. For end group structure determination, a low \bar{M}_n (dp 5) sample of PMMA was prepared by the same procedure with 2 mmol of **10** and 10 mmol of MMA. ^1H NMR (360 MHz, CDCl_3 , J in hertz): δ 5.5–5.7 (m, 1 H, $=\text{CH}$), 4.95–5.1 (m, 2 H, $=\text{CH}_2$), 4.055 (q, $J = 7$, 2 H, OCH_2), 2.85–3.1 (m, 1 H, CHCOOR).

End Group Analysis of PMMA Initiated with 11. See Table II, entry 3. ^1H NMR (360 MHz, CDCl_3): δ 5.0 (m, E and D, 72%), 4.1 (m, A, 72%), 4.3 (m, C, 28%), 2.5 (m, B, 28%).



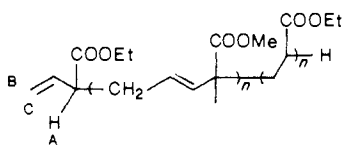
End Group Analysis of PMMA Initiated with 12. See Table II, entry 4. The trimethylsilyl end group was removed by hydrolysis with aqueous methanolic HCl to produce a terminal carboxylic acid. ^1H NMR (360 MHz, CDCl_3): δ 5.6 (m, 1 H, $=\text{CH}$), 4.9–5.1 (m, 2 H, $\text{C}=\text{CH}_2$).

End Group Analysis of PMMA Initiated with 13. See Table II, entry 5. ^1H NMR (360 MHz, CDCl_3): δ 6.74 (m, A, 29%), 5.8–5.95, 6.05–6.15 (2 m, C and C', 71%), 5.04–5.15 (m, D and E, 71%), 2.48 (m, B, 29%). Irradiation of the 5.04–5.15 ppm resonance decoupled both the 5.8–5.95 and the 6.05–6.15 ppm resonances. The relative intensities of the two resonances are 1.7 and 1, respectively.



End Group Analysis of PMMA Initiated with 14. See Table II, entry 7. $^1\text{H NMR}$ (360 MHz, CDCl_3): δ 4.1 (m, 2 H, OCH_2), 5.01 (d, $J = 12$ Hz, 1 H, $\text{C}=\text{CH}_2$ cis H), 5.12 (d, $J = 17$ Hz, 1 H, $\text{C}=\text{CH}_2$ trans H), 5.38-5.6 (m, 1 H, $\text{C}=\text{CH}$), 5.9-6.3 (2 m, 2 H, $\text{C}=\text{CH}$), 3.0 (m, 1 H, methine CH).

End Group Analysis of Poly-2 Initiated with 10. To a solution of 0.22 mL (1 mmol) of 10 and 50 μL of tetrabutylammonium *m*-chlorobenzoate (0.1 M in THF) in 10 mL of THF was added 1.01 g (1.06 mL, 8 mmol) of 2. When the exothermic reaction was finished, 0.86 mL (8 mmol) of ethyl acrylate was added. Then 1 mL of methanol was added, and the solution was evaporated to 1.9 g of oily poly(methyl 2-methylpentadienoate-*b*-ethyl acrylate). GPC: \bar{M}_n 1980, \bar{M}_w 4400, $P = 2.23$ (theory, \bar{M}_n 1900). $^1\text{H NMR}$ (360 MHz, CDCl_3): δ 3.0 (m, 1 H, A), 5.05-5.16 (m, 2 H, B and C). The molar ratio of ethyl acrylate units and methyl 2-methylpentadienoate units is 1.0.



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Registry No. Poly-1, 26985-69-3; (1)(MMA) (block copolymer), 115078-18-7; 2, 86952-00-3; poly-2, 115078-14-3; (2)(MMA) (block copolymer), 115078-19-8; (2)(MMA) (copolymer), 115078-20-1; poly-3, 115078-15-4; poly-4, 33774-25-3; (4)(MMA) (copolymer), 115078-21-2; (4)(MMA) (block copolymer), 115078-22-3; poly-5, 63747-18-2; 6, 115078-12-1; poly-6, 115078-17-6; 7, 31469-15-5; 9, 51425-66-2; 10, 73311-50-9; 11, 73311-52-1; 12, 87121-06-0; 13, 115078-10-9; 14, 115078-11-0; 15, 80-62-6; 16, 115078-13-2; MMA, 80-62-6; PMMA, 9011-14-7; TASF, 59218-87-0; TASHF₂, 85248-37-9; Bu₄NOAc, 10534-59-5; Bu₄NmCB, 60619-92-3; Bu₄NBB, 115116-46-6; 2-(diethylphosphono)-4-butyrolactone, 2907-85-9; sorbaldehyde, 142-83-6; poly(methyl sorbate), 30813-48-0.

Highly Enantioselective and Substrate-Selective Polymers Obtained by Molecular Imprinting Utilizing Noncovalent Interactions. NMR and Chromatographic Studies on the Nature of Recognition

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Abstract: By use of the molecular imprinting technique, highly enantioselective and substrate-selective polymers were prepared by utilizing noncovalent interactions between the print molecule (*L*-phenylalanine derivatives) and methacrylic acid monomers. In the chromatographic mode, such polymers resulted in almost base-line separation of the enantiomers of the respective print molecule (phenylalanine anilide) with a maximum separation factor (α) of 3.5. The polymers also showed a high capacity (1.5 mg of racemate/g of polymer with optically pure peak maxima). Substrates other than the respective print molecule were in most cases poorly resolved. The selectivity was shown to be governed by the number and nature of interactions between the substrate and the polymer stationary phase, as well as the shape and rigidity of the substituents of the print molecule. In order to investigate these interactions, a chromatographic and $^1\text{H NMR}$ study involving titration of the print molecule (phenylalanine anilide) with carboxylic acid was performed. The results were consistent with the existence of multimolecular complexes formed by electrostatic and hydrogen-bonding interactions and allowed an estimation of their formation constants and distribution. From this information, it was concluded that complexes between *L*-phenylalanine anilide and a maximum of three methacrylic acid monomers exist in solution prior to polymerization. On the basis of hydrogen bond theory, a model of the 1:2 complex is proposed. Finally, evidence is presented that is consistent with the existence of shape-specific cavities within the polymer.

The technique of molecular imprinting, that is, producing imprints of molecules in synthetic polymers, has received much attention in recent years. Apart from the general theoretical interest in this technique, potential practical applications are obvious, notably the use of such polymers for separations, facilitated synthesis, and possibly also as enzyme or receptor mimics. In most of the studies reported to date, the molecule forming the cavity (the print molecule) is allowed to interact with functionalized monomers prior to polymerization. After polymerization, the print molecule is removed and subsequent recognition occurs via a combination of reversible binding and shape complementarity. Essentially two different approaches have been followed in these studies: (a) Reversible covalent binding of the print molecule to the monomers has been used. Following this technique numerous

reports have appeared describing highly selective polymers.¹ (b) Functionalized monomers are allowed to "prearrange" around the print molecule by noncovalent interactions (i.e., electrostatic, hydrophobic, hydrogen bonding).²

Whereas approach a has been used for the separation of the enantiomers of sugar derivatives,^{1,3} approach b has in this and in other reports by us been applied in the separation of the enantiomers of amino acid derivatives.^{4,5} Following both approaches, a variety of polymers have been used, encompassing styrene-

(1) See review: Wulff, G. In *Polymeric Reagents and Catalysts*; Washington DC, 1986; pp 186-230, and references cited therein.

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