New Structural and Mechanistic Chemistry in Polymerizations of Vinyl Chloride Initiated by Di-*tert*-alkylmagnesiums

G. M. Benedikt, R. J. Cozens, B. L. Goodall, and L. F. Rhodes*

BFGoodrich Company, Research and Development Center, Brecksville, Ohio 44141

M. N. Bell and A. C. Kemball

European Vinyls Corporation (UK) Ltd., Runcorn, Cheshire WA7 4QD, United Kingdom

W. H. Starnes, Jr.*

Applied Science Ph.D. Program and Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23187-8795

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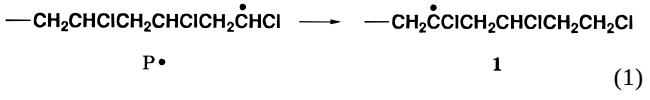
ABSTRACT: The bulk polymerization of vinyl chloride initiated by di-*tert*-butyl- or *tert*-butyl-*tert*-pentylmagnesium etherate gives poly(vinyl chloride) (PVC) specimens containing considerable amounts of cyclopropyl, *trans*-2-*tert*-butylcyclopropyl, and -CHClCH=CH_2 chain ends. This result has no structural precedents among PVC samples that are made by conventional free-radical methods. Formation of the unusual end groups has been rationalized in terms of reactions of various polymeric intermediates having Mg−C bonds, and ethylene formed *in situ* has been shown to be involved in the process that produces the cyclopropyl chain end. Also observed is a *trans*-*t*-BuCH=$CHCH_2$− terminus, whose presence has not been explained. When the polymerization temperature is raised in stages from −20 to 40 °C, the unusual chain ends are gradually replaced by structures that are known to result from reactions of free macroradicals. The various end groups were characterized by high-field NMR techniques. These were applied to both original and Bu_3SnH-reduced PVC specimens, as well as to synthesized end-group models that were used for reference purposes.

Over the last 5 decades, poly(vinyl chloride) (PVC) has become one of the world's most important commodity plastics. Although several commercial methods are used to produce it (suspension, emulsion, mass, and microsuspension polymerization), all of them are based on free-radical chemistry. Unlike polyolefin synthesis, which has undergone several major advances in initiation or catalysis technology during this half century, PVC production still relies entirely on free-radical initiation.

A structurally ideal PVC molecule would consist exclusively of a head-to-tail arrangement of vinyl chloride (VC) units. However, PVC is far from ideal. It contains several structural irregularities, or defects, that have been identified from the ^{13}C and ^{1}H NMR spectra of both reductively dechlorinated PVC and PVC itself.[1]

The normal mode of addition of VC to the growing macroradical (P•) is head-to-tail. Occasionally, though, a head-to-head emplacement occurs. It leads to the formation of chloromethyl (MB) or 1,2-dichloroethyl (EB) branch structures and chloroallylic chain ends (A1/A2), via the reactions in Figure 1.[1c,2] In addition, PVC contains branch structures that are associated with tertiary chloride. They include the 2,4-dichloro-*n*-butyl branch (BB) assemblage that is created by reactions 1 and 2,[1,3] as well as long-branch moieties that result from



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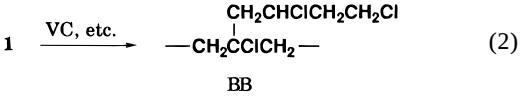
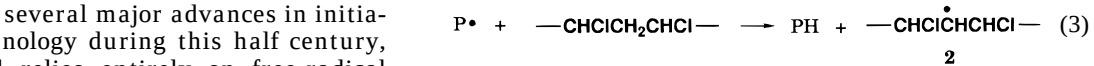


(2)

an analogous process involving H abstraction by P• from backbone CHCl segments that are distant from chain ends.[1] If P• abstracts hydrogen from a methylene group instead (eq 3), an internal allylic (IA) structure can be formed, as well (eq 4).[1c,2,4]



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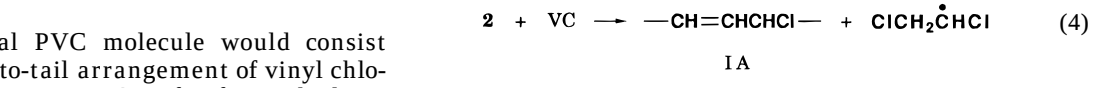

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When PVC is heated, loss of HCl begins much more readily from IA and the tertiary-chloride-containing segments than from the other parts of the polymer.[1b,c] For that reason, these defect sites are effective initiators for the sequential dehydrochlorination of adjacent VC units, a process that generates conjugated polyenes and thus leads to color development.[1b,c] Since all of the labile defects are produced by free-radical chemistry, the development of a non-free-radical route to PVC would seem to be a worthwhile goal from the standpoint of stability improvement. Attainment of this objective also might lead to PVC specimens whose properties have been changed considerably in other useful ways.

Alkylmagnesium compounds are known to initiate the anionic polymerization of a number of vinyl monomers.[5] With that behavior in mind, we have studied the polymerization of VC initiated by di-*tert*-alkylmagnesiums, and we are reporting here an investigation of the end-group microstructures of the resultant resins. This work has provided convincing evidence for the formation of novel PVC end groups by non-free-radical routes.

Results

Synthesis of Organomagnesium Initiators. The initiators were made by a straightforward metathetical procedure involving the addition of a pentane solution

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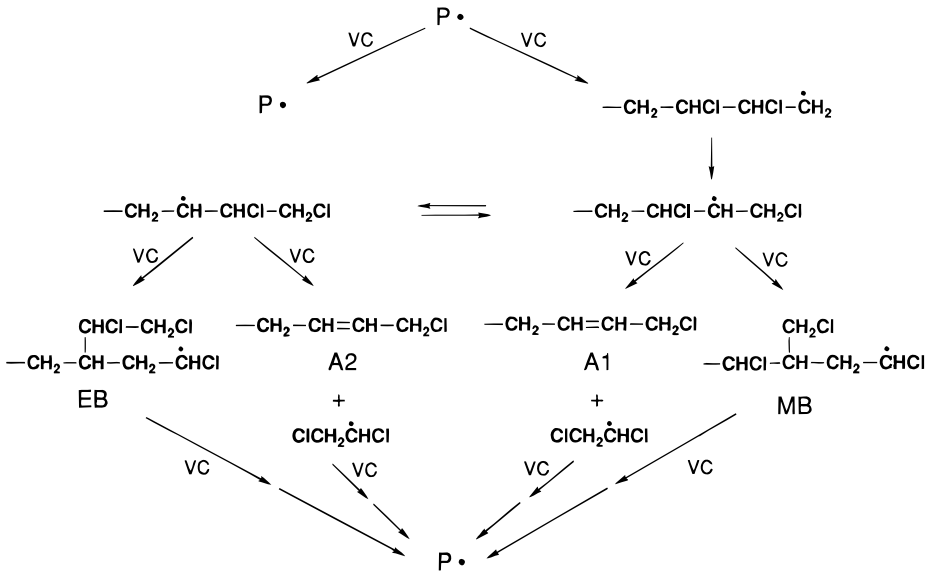


Figure 1. Structures resulting from head-to-head emplacement of monomer during the free-radical polymerization of VC, where P• is the ordinary head-to-tail macroradical.

of *t*-BuLi to an ether solution of a Grignard reagent (eq 5). After workup, $(t\text{-Bu})_2$Mg was obtained as an off-

$$t\text{–BuLi} + \text{RMgCl} \xrightarrow[\text{Et}_2\text{O}]{\text{pentane,}} t\text{–BuMgR} + \text{LiCl} \qquad (5)$$

white waxy solid. The *t*-Bu-*t*-Pe compound was isolated as a pale yellow oil. Both substances were miscible with hydrocarbons, though small amounts of insoluble material (presumably LiCl) were observed occasionally when the isolation had not been done with sufficient care.

The initiators were characterized by ^{1}H NMR spectroscopy, which showed that the $(t\text{-Bu})_2$Mg was complexed with 1.8−2.0 equiv of ether, the exact amount being dependent upon the length of the evacuation period during workup. From 1.3 to 1.6 equiv of ether was present in the *t*-Bu-*t*-Pe complex. Both of the complexes are presumed to be dynamic, because the 500-MHz ^{1}H NMR resonances of the *t*-Bu-*t*-Pe compound became sharp and well-resolved only upon warming to 50 °C.

Proton NMR Spectrum of Commercial PVC. Several structures occurring in "conventional" PVC have been characterized previously by ^{1}H NMR.[1b,4,6] Figure 2A shows the downfield region of the 500-MHz ^{1}H NMR spectrum of a commercial resin. Here, assignments have been made for a number of "defect" segments. In contrast, the 0.0−0.7-ppm region of this spectrum (Figure 3A) is rather featureless. Figures 2A and 3A and their assignments comprise a baseline against which the spectra of the organomagnesium-initiated resins can be compared.

Polymerizations. Table 1 summarizes the conditions and results of several VC polymerizations that were initiated by the organomagnesium compounds. The copolymerization experiments (runs 9−11, 15, and 16) were performed to obtain mechanistic understanding and are discussed in detail in subsequent sections.

Spectral Characterization of Cyclopropane Groups and Head Groups in *tert*-Butyl-*tert*-pentylmagnesium-Initiated PVC. Figure 4 shows the high-field region of the ^{1}H NMR spectrum produced by the polymer made in run 1 of Table 1. The triplet at 0.86 ppm has been assigned to the ethyl CH_3 protons in a *tert*-pentyl moiety that is presumed to be a head

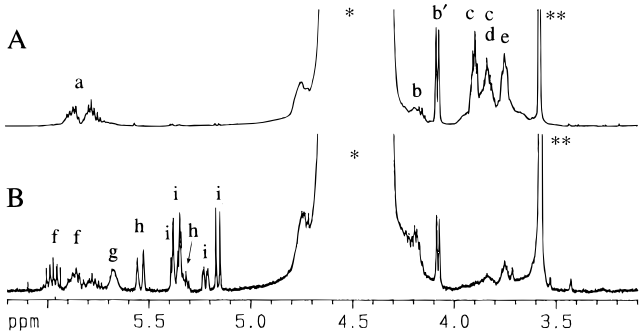


Figure 2. Partial ^{1}H NMR spectra (500.14 MHz, THF-d_8, 50 °C) of (A) commercial PVC and (B) $(t\text{-Bu})_2$Mg-initiated PVC. Assignments: a, −C*H*=C*H*CH_2Cl and −CH_2C*H*=C*H*CHCl−;[4] b and b′, *cis*- and *trans*-CH=CHCH_2Cl, respectively;[4,6a] c, −CHClCH_2Cl;[6a,b] d, −CH_2Cl branch;[6a,b] e, −CH_2CH_2Cl;[6a,b] f, −CHClC*H*=CH_2;[6b] g, *trans*-CH_2C*H*=C*H*CH_2−;[6c] h, *trans*-C*H*=C*H*C$(CH_3)_3$; i, −CHClCH=CH_2;[6b] *, principal backbone −C*H*Cl−; **, solvent.

group rather than a tail group formed by chain termination. The CH_2 protons of this group appear as a complex multiplet centered at ca. 1.32 ppm, while its remaining CH_3 protons resonate at 0.95−0.97 ppm and appear as a three-line pattern when the spectrum is expanded. The complexity of this pattern and that of the CH_2 protons results from nonequivalence that is caused by the presence of the −CHCl− chiral centers along the polymer backbone.

A *tert*-butyl moiety which also is presumed to be a head group produces a four-line pattern (after expansion) that is centered at ca. 1.01 ppm. Thus four distinct *tert*-butyl groups are being resolved in this region, a result which implies that their ^{1}H NMR chemical shifts also are being influenced by the configurations of the proximal VC units. That is, the chiral −CHCl− moieties of three such units can have meso (*m*) or racemic (*r*) emplacements which generate four sterically unique triads: *mm*-, *mr*-, *rm*-, and *rr*-*t*-Bu.

Figures 3B and 4 show two new sets of resonances that are centered at about 0.13 and 0.50 ppm and do not appear in the spectrum (Figure 3A) of the commercial PVC sample. These chemical shifts are consistent with the presence of cyclopropane moieties, but the

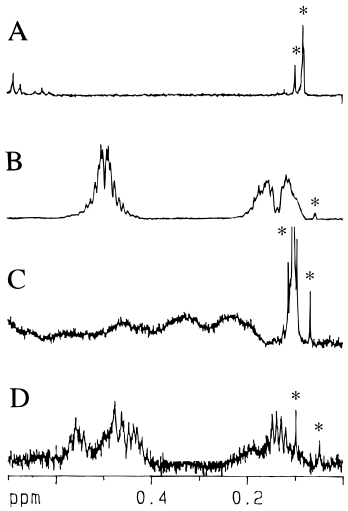


Figure 3. Partial ^{1}H NMR spectra (500.14 MHz, THF-d_8, 50 °C) of (A) commercial PVC, (B) *t*-Bu-*t*-PeMg-initiated PVC, (C) Zn-treated commercial PVC, and (D) (*t*-Bu)$_2$Mg-initiated PVC. *, silicone grease.

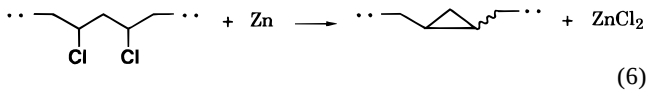
Table 1. Results of Some Di-*tert*-alkylmagnesium-Initiated (Co)Polymerizations of VC

run[a]	initiator[b]	comonomer[c]	temp, °C	VC conversion, %	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
1	BuPe		−20	2.8	5.71	27.8
2	BuPe		−20	2.5	5.43	19.9
3	BuPe		0	12	11.5	50.0
4	BuPe		0	11.3	10.9	41.8
5	BuPe		20	40.7	31.8	204
6	BuPe		20	39.5	34.3	165
7	BuPe		40	29	21.0	120
8	BuPe		40	29	18.7	90.5
9	BuPe	ethylene	0	7.6	12.2	38.3
10	BuPe	ethylene	0	12.4	14.4	51.1
11	BuPe	ethylene-d_4	0	8.2	11.9	40.2
12	BuBu[d]		−20	2.7		
13	BuBu		20	37	16.2	102
14	BuBu		20	33	16.8	84.4
15	BuBu	neohexene	20	19	18.8	97.1
16	BuBu	isobutene	20	16	12.6	38.4

[a] Reaction time = 24 h. [b] BuPe = *t*-Bu-*t*-PeMg; BuBu = (*t*-Bu)$_2$Mg. Concentration = 0.2 mol % relative to VC, except where noted otherwise. [c] Concentration = 10 wt % relative to VC. [d] Concentration = 0.1 mol % relative to VC.

question remains as to whether these groups are internal or are present at chain ends.

Cais and Spencer[7] used NMR techniques to study the formation of main-chain cyclopropane groups in PVC that had been treated with zinc (eq 6). We have applied



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their treatment procedure to a commercial resin and have found that the cyclopropyl ^{1}H NMR resonances of the product are completely inconsistent with those arising from our organomagnesium-initiated samples of PVC. Compare, for example, the spectra of Figure 3B,C. In the latter spectrum, backbone cyclopropane signals appear between ca. 0.15 and 0.7 ppm, but their exact chemical shifts and general appearance differ very significantly from those of the signals in Figure 3B.

Confirmatory evidence for the absence of backbone cyclopropanes was provided by the ^{13}C{^{1}H} NMR spectrum of a Bu_3SnH-reduced[1a,8] PVC sample that had been made by initiating with *t*-Bu-*t*-PeMg at −20 °C. This "polyethylene" spectrum did not exhibit resonances at ca. 11.4, 12.3, 16.0, and 19.2 ppm, which were the values to be expected[7] for the ring carbons of isolated cis- and trans-disubstituted cyclopropanes in the main chain of the polymer.

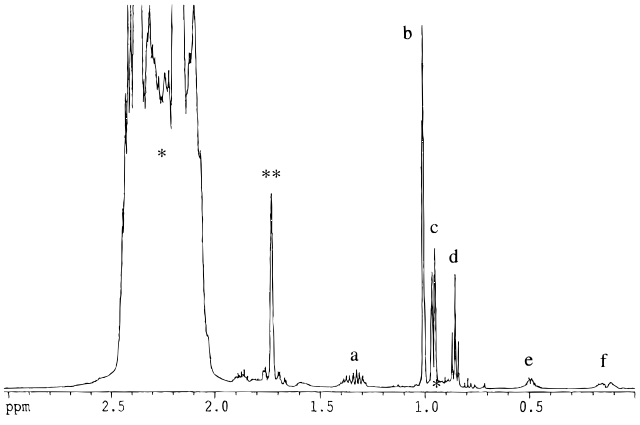
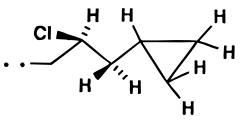


Figure 4. Partial ^{1}H NMR spectrum (500.14 MHz, THF-d_8, 50 °C) of *t*-Bu-*t*-PeMg-initiated PVC. Assignments: a, $CH_3CH_2C(CH_3)_2CH_2CHCl-$; b, $(CH_3)_3CCH_2CHCl-$; c, $CH_3-CH_2C(CH_3)_2CH_2CHCl-$; d, $CH_3CH_2C(CH_3)_2CH_2CHCl-$; e and f, cyclopropane protons; *, principal backbone $-CH_2-$; **, solvent.

In order to determine the exact nature of our cyclopropane end groups, a variety of NMR techniques was used. Integration revealed that the multiplets centered in Figure 3B at ca. 0.13 and 0.50 ppm are approximately equal in intensity. The correlation spectroscopy (COSY) 2D ^{1}H NMR spectrum of the sample producing these peaks (Figure 5) shows that there is another upfield resonance at ca. 0.9 ppm to which these resonances are coupled. The 0.9-ppm signal can be ascribed to the methine proton of a monosubstituted cyclopropane, and it is coupled, in turn, to a broad resonance centered near 1.6 ppm which can be assigned to the diastereotopic protons of a methylene group attached to a cyclopropane ring carbon. End group **3** is the structure that these



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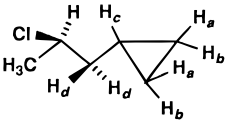


4

findings implicate, and it closely resembles the model compound, **4**, whose ^{1}H NMR resonances have been assigned[9] as follows: δ 0.40 (H_a), 0.00 (H_b), 0.85 (H_c), and 1.55 ppm (H_d). These values compare very favorably with those found by us for **3**.

The cyclopropane end group undoubtedly is not chlorinated, for if it were, the proton(s) on its chlorinated carbon(s) would have experienced large downfield shifts. In the case of 1-chloro-2-ethylcyclopropane, for example, the C*H*Cl signal of the cis- and trans-isomers appears at 3.15 and 2.73 ppm, respectively.[10] Moreover, the inverse heteronuclear correlation (HETCOR) ^{13}C−^{1}H NMR spectrum shown in Figure 6A reveals that the two upfield cyclopropyl proton resonances of the end group are coupled to the *same* carbon resonance, which appears near 4.5 ppm. Finally, it should be noted that the chlorinated-carbon resonance appears far downfield (at 34.1 and 32.6 ppm, respectively) in the ^{13}C NMR spectra of *cis*- and *trans*-1-chloro-2-ethylcyclopropane.[10]

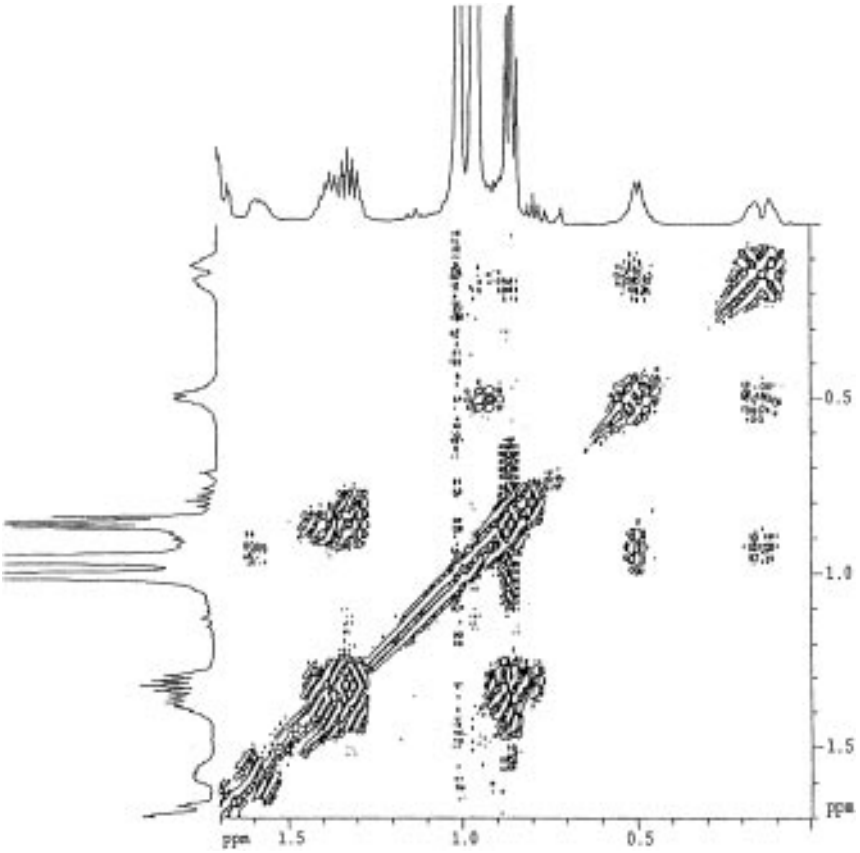
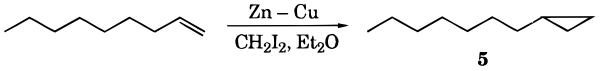


Figure 5. Phase-sensitive COSY 2D ^{1}H NMR partial spectrum (500.14 MHz, THF-d_8, 50 °C) of *t*-Bu-*t*-PeMg-initiated PVC.

Additional structural evidence pertaining to the cyclopropane chain end was obtained from the ^{13}C NMR spectrum, referred to above, of our Bu_3SnH-reduced sample of *t*-Bu-*t*-PeMg-initiated PVC. That spectrum displayed resonances at 11.26 and 4.74 ppm in the intensity ratio of 1:2, respectively, that was expected for the *C*H and *C*H_2 ring carbons of a (long *n*-alkyl)-cyclopropane. These shift values were noted to resemble those of the analogous carbons of *n*-pentylcyclopropane (10.9 and 4.3 ppm, respectively[11]), but comparisons with the shifts of a better model were desired. Such a model (**5**) was obtained by the cyclopropanation of 1-nonene according to the Simmons−Smith procedure[12] (eq 7).



(7)

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The ^{13}C{^{1}H} NMR spectrum of **5**, recorded under the conditions that had been used for the dechlorinated PVC specimen, showed peaks at 11.24 and 4.72 ppm, the respective intensities of which also were in the required ratio of 1:2. Since these shift values and those of the reduced polymer (see above and Table 2) are identical within the limits of experimental error, the evidence for the presence of **3** in the original (unreduced) PVC sample now seems incontrovertible. In subsequent sections we will show that other unusual end groups also occurred in this polymer.

Spectral Characterization of Cyclopropane Groups and Head Groups in Di-*tert*-butylmagnesium-Initiated PVC. Figure 3D shows a part of the ^{1}H NMR spectrum obtained for a polymer made by initiating with (*t*-Bu)$_2$Mg (0.2 mol %) at −20 °C. Except for the use of a 90-h reaction period, the polymerization conditions were identical to those selected for the preparation of the resin, discussed above, that was made with *t*-Bu-*t*-PeMg. In addition to the four-line pattern expected (*vide supra*) for the *tert*-butyl head group (which, however, is not depicted here), the spectrum shows broad, ill-defined signals at 0.1−0.2 and 0.4−0.6 ppm that are different, for the most part, from the resonances in Figure 3B, though there are components which are common to both traces. Thus the (*t*-Bu)$_2$Mg-initiated polymer seems to contain more than one type of cyclopropane moiety, a supposition that has been verified by the HETCOR 2D NMR spectra displayed in Figure 6. These spectra clearly show that **3** predominates greatly in the *t*-Bu-*t*-PeMg-initiated resin (as discussed above) and that the (*t*-Bu)$_2$Mg-initiated sample apparently contains both **3** and another cyclopropane structure that correlates with a carbon signal near 8.0 ppm. The "new" cyclopropane also exhibits correlation peaks with a carbon resonance occurring at ca. 31 ppm.

Characterization of the new cyclopropane required an approach which was similar to that described in the previous section. First, Bu_3SnH was used to reduce another sample of (*t*-Bu)$_2$Mg-initiated PVC prepared at −20 °C, and the ^{13}C{^{1}H} NMR spectrum of the reduced polymer was recorded. This spectrum contained not only the resonances of reduced **3** (at 4.72 and 11.23 ppm) but also new signals at 8.14 and 14.85 ppm that were thought to arise from the other cyclopropane (see Table 2). Reexamination revealed that the latter peaks also were present, though at relatively low intensities (see Table 2), in the ^{13}C{^{1}H} NMR spectrum of the *t*-Bu-*t*-PeMg-initiated sample reduced with Bu_3SnH.

In order to identify conclusively the new cyclopropane moiety, two additional model substances were prepared for reference purposes. The trialkylcyclopropane **6** was obtained from a Simmons−Smith reaction of a com-

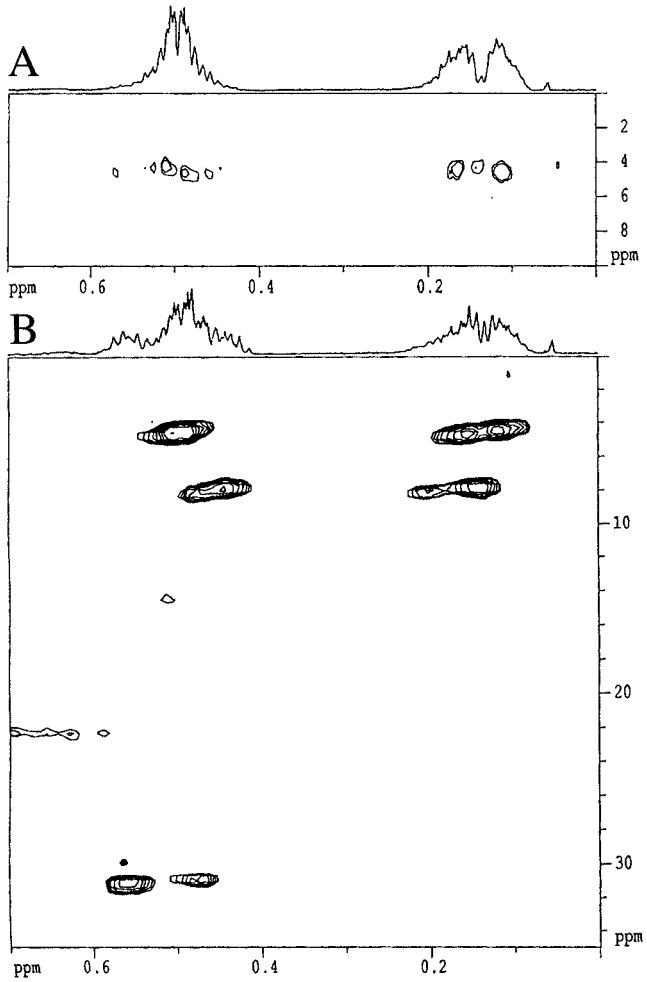
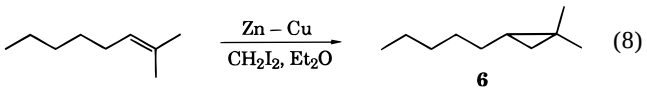


Figure 6. HETCOR 2D $^{13}C-^{1}H$ NMR partial spectra (125.77 and 500.14 MHz, THF-d_8, 50 °C) of (A) *t*-Bu-*t*-PeMg-initiated PVC and (B) an acetone extract of (*t*-Bu)$_2$Mg-initiated PVC.

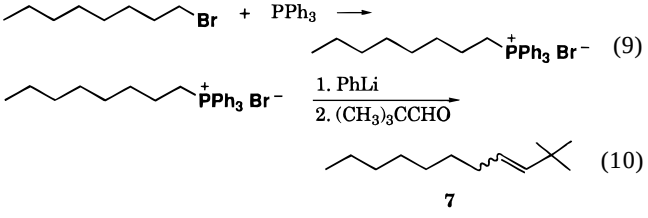
mercially available alkene (eq 8) and characterized by



6 (8)

both ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR peak assignments were confirmed by the results of distortionless enhancement by polarization transfer (DEPT) experiments, and the shifts of the diagnostic carbon resonances are given in Table 2.

A Wittig synthesis (eqs 9 and 10) was used to prepare an alkene precursor (**7**) for the other cyclopropane that



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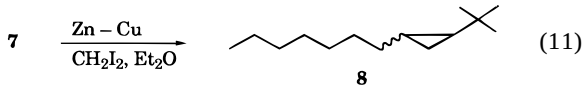
was desired. (An alternative preparation of **7**, described in the Experimental Section, involved the reaction of *n*-octanal with a Wittig reagent formed from PhLi and neopentyltriphenylphosphonium iodide.) Proton NMR analysis showed that **7**, obtained from reaction 10, was an 84:16 mixture of stereoisomers in which the predominance of the cis-isomer was revealed by the relative magnitudes of the vicinal coupling constants of the alkene protons ($J_{cis} < J_{trans}$).[13] Simmons–Smith cyclopropanation of **7** (eq 11) gave compound **8** as a mixture



8 (11)

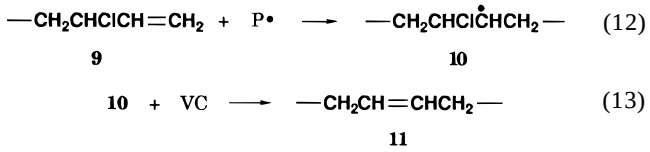
for which the stereoisomeric composition was shown by NMR analysis to be ca. 75:25 cis:trans. Table 2 lists the chemical shifts of the diagnostic carbon resonances of *trans*-**8**.

From the information in Table 2 and the discussion above, it follows that the two end groups modeled by **5** and *trans*-**8** were present in both of our reduced samples of PVC. Neither of these samples contained detectable amounts of the end groups modeled by *cis*-**8** and **6**, and interestingly, as Table 2 demonstrates, the relative yield of the monoalkylcyclopropane end was much greater when the initiator for polymerization was *t*-Bu-*t*-PeMg rather than (*t*-Bu)$_2$Mg.

Spectral Characterization of Alkene End Groups in Di-*tert*-alkylmagnesium-Initiated PVC. Figure 2B shows the downfield region of the ^{1}H NMR spectrum of a (*t*-Bu)$_2$Mg-initiated resin made at −20 °C (run 12, Table 1). Except for the main-chain C*H*Cl signal, the signals for A1/A2 and IA at ca. 4.05–4.15 and 5.75–5.95 ppm, and the $-CH_2CH_2Cl$ triplet at 3.75 ppm, this trace bears little resemblance to the one for a commercial PVC that appears in Figure 2A. The resonances for 1,2-dichloroethyl and MB groups (peaks c and d, respectively) are very weak or nonexistent in Figure 2B, but that spectrum displays several new signals in the alkene region between ca. 5.1 and 6.0 ppm.

Recent publications[6b,14] have been concerned with the possible presence of the vinyl end group, $-CHClCH{=}CH_2$ (**9**), in PVC. The occurrence of **9** in the polymer has been confirmed by the NMR spectra of a synthesized model,[6b] but in commercial resins this structure seldom is seen and ordinarily is detectable only in fractions with low molecular weights.[14] However, Figure 2B reveals the presence of an extraordinarily large amount of **9** in the (*t*-Bu)$_2$Mg-initiated polymer and gives the assignments (f and i) for its alkene proton resonances. Other ^{1}H NMR spectra showed that major amounts of **9** occurred in our *t*-Bu-*t*-PeMg-initiated resins, as well.

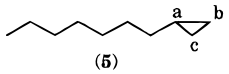
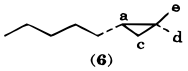
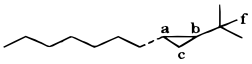
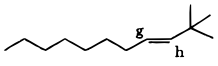
In another recent article,[6c] **9** has been shown to be the precursor of an internal alkene moiety (**11**) that is formed via reactions 12 and 13 and is responsible for



the broad singlet (g) which appears in Figure 2B at 5.67 ppm.

The remaining alkene signals (h) in Figure 2B (the doublet at 5.55 ppm and the overlapping multiplet centered at 5.33 ppm) have been assigned to a *trans*-*t*-BuCH=CHCH$_2$– end group (**12**). From a 2D COSY spectrum (not included here), it was evident that these two resonances were coupled to one another and that the 5.33-ppm multiplet also was coupled to a methylene proton resonance at ca. 2.2 ppm. Two broad signals at 0.851 and 0.857 ppm were assignable to the *t*-Bu protons of **12**. In order to verify the existence of that structure, the $^{13}C\{^{1}H\}$ NMR spectrum of the Bu_3SnH-reduced

Table 2. Selected ^{13}C NMR Chemical Shifts of Model Compounds and Bu_3SnH-Reduced PVC Resins

substance	δ,[a] ppm vs Me_4Si							
	a	b	c	d	e	f	g	h
 (**5**)	11.24	4.72	4.72					
 (**6**)	25.48		20.42	20.02	27.71			
 (*trans*-**8**)	14.87	28.72	8.15			28.68		
 (*trans*-**7**)							125.3	141.9
reduced PVC[b]	11.26(29)[c]	4.74	4.74					
	14.88(4)[c]	*d*	8.16			28.75		
							125.3	141.8
reduced PVC[e]	11.23(3)[c]	4.72	4.72					
	14.85(4)[c]	*d*	8.14			28.73		
							125.3	141.8

[a] See Experimental Section for details. [b] For PVC preparation conditions, see runs 1 and 2 in Table 1. [c] Peak area relative to principal $-CH_2-$ area of 10^4. [d] Assignment uncertain. [e] For PVC preparation conditions, see run 12 in Table 1.

polymer made with $(t\text{-Bu})_2Mg$ was compared to that of the two **7** isomers. The comparison (see Experimental Section and Table 2) showed that the dechlorinated resin did indeed incorporate the end group modeled by *trans*-**7** but contained the less thermodynamically stable cis-end in only a very low concentration, if at all. Thus the occurrence of two *t*-Bu ^1H signals near 0.85 ppm must be ascribed to an effect of chain tacticity on the spectrum of the unreduced trans-structure, rather than to the presence of both that structure and the stereoisomeric cis-end.

Analyses by NMR revealed that **12** also was present in the *t*-Bu-*t*-PeMg-initiated polymers made at −20 °C.

Analysis of a VC Polymerization by GC. Gas chromatography was used to analyze the head space of a polymerization initiated by $(t\text{-Bu})_2Mg$ at 0 °C. The results revealed the presence of ethylene, isobutene, and "neohexene" (3,3-dimethyl-1-butene). Since the detection of these substances raised the possibility of their incorporation into the polymer, studies were undertaken in order to determine their effects on polymerizations.

***tert*-Butyl-*tert*-pentylmagnesium-Initiated Copolymerization of Ethylene with VC.** Copolymerizations of ethylene and VC were attempted by using *t*-Bu-*t*-PeMg for initiation at 0 °C. Some of the results are presented in Table 1, where runs 3 and 4 are controls performed with different batches of initiator, and runs 9−11 are experiments in which ethylene or ethylene-d_4 was used. In the case of runs 9 and 10, ^1H NMR analysis revealed the incorporation of significant amounts of ethylene into the main chain of the polymers.

Integrations of the cyclopropyl proton resonance near 0.5 ppm showed that the presence of ethylene had not increased the relative amount of chain end **3** (cf. Figure 7A,B). On the other hand, the addition of ethylene-d_4 caused the cyclopropyl region of the spectrum to undergo drastic changes in peak shapes and intensities (see

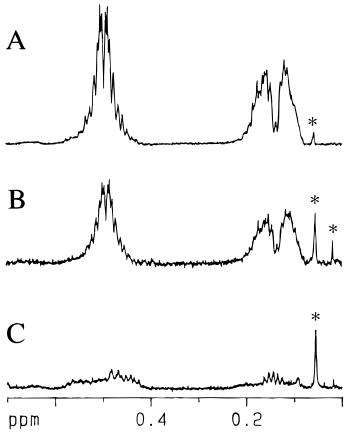


Figure 7. Partial ^1H NMR spectra (500.14 MHz, THF-d_8, 50 °C) of *t*-Bu-*t*-PeMg-initiated PVC made with (A) no comonomer addition, (B) ethylene addition, and (C) ethylene-d_4 addition. *, silicone grease. All of the spectra have been printed with the resonances scaled to the same principal $-CH\text{Cl}-$ intensity. The molecular weights of the polymers were approximately the same.

Figure 7C) which were indicative of comonomer incorporation into the three-membered ring. Additional support for such incorporation was provided by a $^{13}C\{^1H\}$ NMR spectrum (not depicted here), which revealed that the use of the deuterated monomer had eliminated the cyclopropyl ring CH_2 signal near 4.5 ppm. This result is quite consistent with the broadening and splitting of a carbon resonance that double deuteration of the carbon is expected to cause. The involvement of ethylene in **3** formation was further confirmed by a ^2H NMR spectrum of the polymer from run 11, which showed two broad and weak signals near 0.1 and 0.5 ppm.

Di-*tert*-butylmagnesium-Initiated Copolymerization of Neohexene with VC. In Table 1, runs 13 and 14 are controls that can be compared with an

experiment (run 15) in which neohexene was used. Although neohexene addition reduced conversion, it did not cause significant changes in the values of M_n and M_w. Thus, like excess ethylene (see Table 1), excess neohexene did not increase the rate at which the growth of polymer chains was stopped. The latter observation was consistent with the ^{1}H NMR spectrum (not shown) of the polymer from run 15. This spectrum revealed no significant enhancements by neohexene of the resonances produced by the *tert*-butylcyclopropane chain end or the terminal *tert*-butylalkene, **12**. However, two weak resonances at 0.931 and 0.943 ppm, assignable to *tert*-butyl protons, were greatly intensified. These signals can therefore be ascribed to the pendent *tert*-butyl moieties of neohexene units in the main chain. The duality of these *tert*-butyl peaks evidently is caused by tacticity.

Di-*tert*-butylmagnesium-Initiated Copolymerization of Isobutene with VC. Run 16 in Table 1 is a copolymerization with isobutene that also can be compared to control runs 13 and 14. Unlike ethylene and neohexene, isobutene significantly decreased both M_n and M_w. The ^{1}H NMR spectrum of the resultant polymer (not shown) contained new peaks between 1.08 and 1.15 ppm that could reasonably be attributed to the methyl protons of isobutene units in the main chain. Integration showed that the concentration of these units was 51.5 per 1000 VC units. On the other hand, isobutene addition did not affect the cyclopropane spectral region. Thus the molecular-weight reduction caused by isobutene was not connected with the formation of cyclopropane termini. The reduction might have resulted, instead, from a chain-transfer process involving the abstraction of allylic hydrogen from isobutene by free or metal-complexed growing-chain macroradicals.

Effect of Temperature on Polymerizations Initiated by *tert*-Butyl-*tert*-pentylmagnesium. The data for runs 1−8 in Table 1 show that polymerizations initiated by *t*-Bu-*t*-PeMg at several temperatures were fairly reproducible with regard to VC conversion and polymer molecular weight. This agreement was especially gratifying because different batches of the initiator had been used. The conversion and molecular weight data have been plotted as functions of temperature in Figures 8 and 9, which show that conversion, M_n, and M_w all attained their maximum values at 20 °C.

Analyses by ^{1}H NMR revealed that the relative amounts of the end groups varied with temperature, as well. This effect is exemplified by the partial spectra in Figure 10, which pertain to the polymers made in runs 3 and 6 of Table 1. These traces indicate that the change from 0 to 20 °C caused the 1,2-dichloroethyl and MB concentrations to increase at the expense of that of the alkene terminus, **9** (and possibly that of end group **12**). Moreover, the upfield regions (not depicted) of the same spectra showed that the temperature increase also reduced the concentrations of the two types of cyclopropane end in these polymers.

Discussion

We are aware of one previous report on VC polymerization initiated by a preformed and purified di-*tert*-alkylmagnesium. The initiator used in that study,[15] (*t*-Bu)$_2$Mg, was completely free of complexed ether, having been synthesized from *t*-BuLi and activated $MgCl_2$ according to a published method.[16] When an ether was not present during the polymerization, the polymer

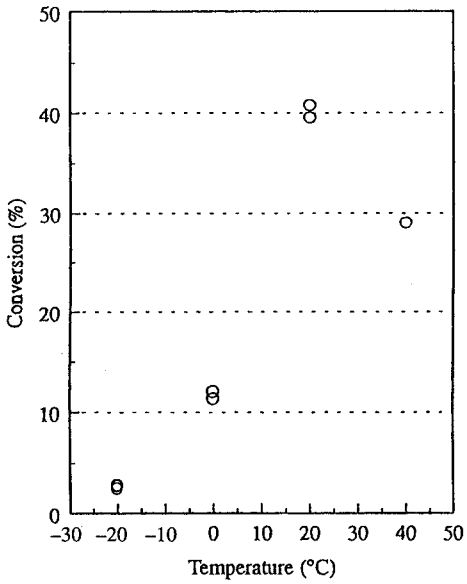


Figure 8. Effect of temperature on conversion during the *t*-Bu-*t*-PeMg-initiated polymerization of VC.

obtained with this initiator was thought to have *tert*-butyl groups at both ends, as in structure **13**.[15] How-

$$(CH_3)_3C(CH_2CHCl)_nC(CH_3)_3$$

13

$$(CH_3)_3C(CH_2CHCl)_nCH_2CH_2Cl$$

14

ever, when THF had been added, the polymer was believed to have structure **14**,[15] and its viscosimetric molecular weight was less than that of the resin made without THF.[15] These results were attributed to the ability of THF to act as a transfer agent in a radical polymerization of VC.[15] That presumption was quite reasonable, for a considerable amount of transfer to THF had, in fact, been detected already by Mickley et al.,[17] who reported that the transfer constant, C_S, of THF is 3×10^{-3} during the free-radical polymerization of VC at 40 °C. On the other hand, no firm conclusions were reached with regard to the mechanism for the (*t*-Bu)$_2$Mg-initiated polymerization of VC in the absence of an ether.[15]

In contrast to the seemingly small amount of published work with (*t*-Bu)$_2$Mg, the *t*-BuMgCl-initiated polymerization of VC was studied extensively in the late 1960s and early 1970s by Guyot et al.[18] These researchers concluded that two polymerization mechanisms were operative with *t*-BuMgCl in THF at 25 °C: a conventional free-radical process and an "ionic" mechanism.[18] Distinguishing features of the "ionic" polymer included a low molecular weight and C=C unsaturation, detected by ^{1}H NMR, which was assumed to be at chain ends.[18] However, no conclusive evidence for an ionic propagation was presented, and in a subsequent study of another PVC specimen that had been made in a very similar manner, analysis by 75-MHz ^{13}C NMR failed to reveal the presence of any C=C termini.[19] An investigation by Minato and co-workers[20] also did not establish the mechanism for the polymerization of VC initiated by *t*-BuMgCl but did reveal some intriguing complexities of the overall process.

In contrast to these findings, the present study shows convincingly that termination reactions mediated by magnesium can occur under our conditions. One of

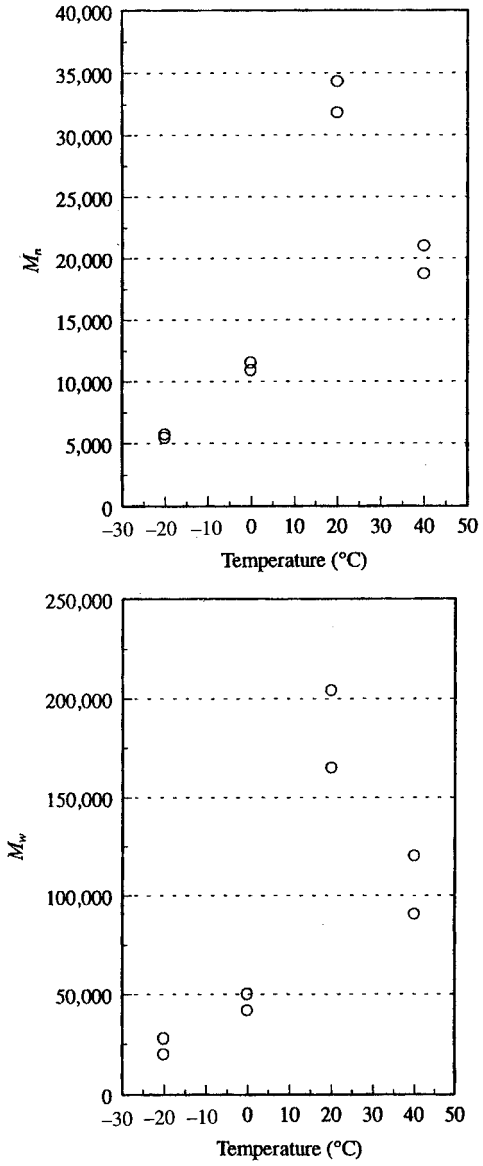


Figure 9. Effect of polymerization temperature on the M_n and M_w of *t*-Bu-*t*-PeMg-initiated PVC.

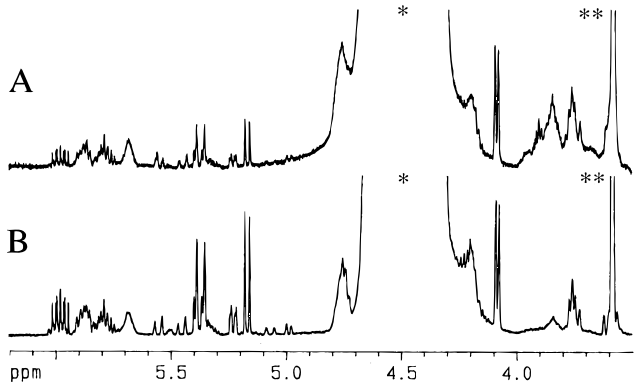
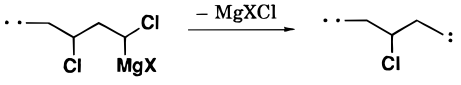


Figure 10. Partial ^{1}H NMR spectra (500.14 MHz, THF-d_8, 50 °C) of *t*-Bu-*t*-PeMg-initiated PVC made at (A) 20 °C and (B) 0 °C. *, principal backbone −C*H*Cl−; **, solvent. The spectra have been printed with the resonances scaled to the same principal −C*H*Cl− intensity.

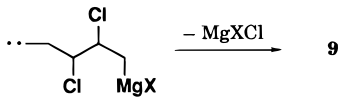
these reactions is the process that produces abnormally high concentrations of the alkene end group, **9**. α-Haloorganomagnesium compounds tend to decompose at low temperatures in order to form carbenes or carbenoid intermediates,[21] and alkyl carbenes frequently experience intramolecular rearrangements that yield alkene products.[22] Hence, a reasonable route to **9** is represented by eq 14, where X is either Cl or an organic radical.



15 (14)

Formation of the precursory structure, **15**, might occur in several ways, one of which is that the polymer chain associates continuously with the magnesium species from the moment of its initiation until its termination. Another possibility is that a radically polymerizing chain terminates to form **15** when it encounters a magnesium species (such as a complex between VC and a magnesium moiety, for example). This suggestion is not as implausible as it first might appear. At the low temperatures of our polymerizations, radical chain transfer to monomer (which ordinarily forms most of the chain ends) is slowed appreciably,[23] and the diffusion rate and concentration of the supposed magnesium terminator may be much higher than those of the growing macroradicals whose interaction also stops chains. If the growing polymer chain does associate continuously with a magnesium moiety, then chain tacticity and reactivity ratios for copolymerization should differ from those encountered in conventional polymerizations of VC. Investigation of these possibilities is under consideration.

Another conceivable pathway to **9** involves the decomposition, via reaction 15, of a species (**16**) that

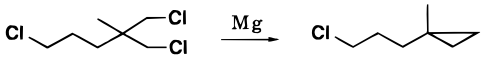


16 (15)

results from a head-to-head VC emplacement. Conceptually, at least, the possible routes to **16** are analogous to those to **15** that were just described. Experiments with isotopically labeled monomer should show which of the two reactions, 14 or 15, actually occurs.

Another unusual chain terminus formed in our polymerizations is the *tert*-butylalkene moiety, **12**. Rather than being an end group, it may be a head group formed by tail addition of a *t*-BuCH=CH$^\bullet$ radical (or *t*-BuCH=CHMgX?) to VC. The mechanism for its generation is, however, not yet apparent.

Model reactions support the view that, in our polymerizations, magnesium involvement also was crucial for the formation of the cyclopropane chain ends. For example, the reaction of magnesium metal with compound **17** gives the corresponding cyclopropane, **18**, via an intermediary organomagnesium chloride (eq 16).[24]

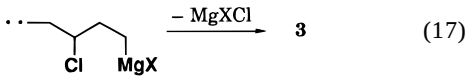


17 **18** (16)

The cyclization of haloorgano magnesiums tends to form cyclopropanes rather than less-strained cyclopentanes,[24] and Grignard reagents are known to be unstable toward cyclopropane formation when they contain chlorine, bromine, or iodine in a 3-position.[21b]

The generation of cyclopropane end group **3** requires not only an association of the growing polymer chain

with a magnesium species but also the presence of ethylene. Thus **3** evidently is formed from **19** in reaction 17. The creation of **19** does not simply involve the



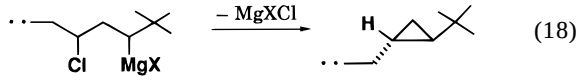
(17)

19

insertion of ethylene into the polymer−Mg bond of **15**, for in that event, ethylene would compete directly with VC for the reactive chain end, and ethylene addition (in runs 9 and 10 of Table 1) would have caused a considerable increase in the number of **3** ends formed. A parallel argument militates against the formation of **19** by a reaction of a magnesium species with the radical, $-CH_2CHClCH_2{}^{\bullet}CH_2$, that would result from the addition of ethylene to an ordinary (P$^{\bullet}$) macroradical.

On the other hand, a plausible explanation, not yet confirmed, for the failure of added ethylene to increase the yield of **3** is that **19** is produced by a reaction of the growing chain with a complex formed from ethylene and a magnesium species. The concentration of this complex must not increase significantly when ethylene is added extrinsically. That condition will be met if the amount of ethylene made *in situ* from the initiator and VC (see below) is sufficient to form the complex in its maximum yield. Although the experiment performed with ethylene-d_4 requires that the complex be made reversibly, the equilibrium constant for its creation must be so large that the yield of the complex is essentially equivalent to the amount of the metal species from which the complex is formed.

Similar statements can be made about the mechanism for the formation of end group **21**, which seems likely to include reaction 18 as the final step. Formation of



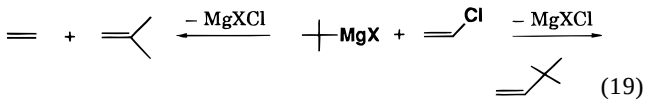
(18)

20 **21**

the precursor, **20**, presumably requires neohexene, but as in the case of end group **3**, the yield of **21** was not enhanced when the requisite alkene was added. The observed incorporation of added ethylene and neohexene into the polymer backbone shows, of course, that termination does not always ensue immediately when these alkenes encounter the growing polymer chain.

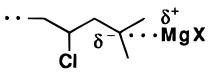
End groups **3** and **21** are very unlikely to have resulted from cycloaddition reactions of a carbene/carbenoid intermediate formed from **15**. A mechanism of this type should have given a chlorocyclopropane end instead, because in our polymerizations, the (vinyl chloride)/alkene mole ratios were very large.

The formation of ethylene, isobutene, and neohexene during (t-Bu)$_2$Mg-initiated polymerization can be ascribed to well-known coupling and disproportionation reactions of organomagnesium compounds,[18,25] as in eq 19. Lack of any conclusive evidence for the presence of

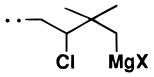


(19)

a terminal cyclopropane derived from isobutene is in line with expectations based on arguments made above. The tertiary carbanionoid intermediate, **22**, a needed pro-



22



23

genitor, would be less stable thermodynamically than the analogous primary and secondary species leading to **3** and **21**, respectively. Moreover, the isomeric precursor, **23**, resulting from inverse addition, would be destabilized strongly by steric repulsions.

Small amounts of transition metals are known to catalyze the coupling and disproportionation reactions of Grignard reagents with organic halides.[25] In an attempt to limit metal impurities in our (t-Bu)$_2$Mg, a batch of this initiator was made from 99.99% pure magnesium without the use of metal syringes or transfer needles. Inspection by NMR showed that the product thus obtained gave a PVC whose microstructure was identical to that of resins made with our "ordinary" (t-Bu)$_2$Mg under the same conditions. However, in striking contrast to this observation, *ether-free* samples of (t-Bu)$_2$Mg, made by a method developed previously,[16b] gave polymer lacking significant amounts of the unusual chain termini, **3**, **9**, **12**, and **21**. The mechanistic significance of this finding remains to be ascertained.

Why was the **3:21** ratio much higher when the initiator was t-Bu-t-PeMg rather than (t-Bu)$_2$Mg, as Table 2 demonstrates? This observation can perhaps be explained, at least partially, by a greater concentration, in the former case, of a metalloethylene complex, considered above, that leads to **3** via **19**. Gas-phase reactivity data suggest that ethyl radicals abstract hydrogen more readily from *tert*-pentyl radicals than from *tert*-butyl radicals.[26] If the behavior of vinyl radicals (free or complexed) derived from VC were similar in these abstractions to the behavior of ethyl radicals, then more metalloethylene might indeed be formed from the t-Bu-t-PeMg. Under these circumstances, the metalloethylene concentration would depend upon the local concentration of the ethylene made *in situ*.

Preferential disproportionation of the *tert*-pentyl group also would tend to prevent the formation of the coupling product, t-PeCH=CH$_2$ (which is analogous to neohexene), and thus might account for our failure to detect the cyclopropane moiety that this alkene should generate. A small amount of such an end group might have been present in some of our t-Bu-t-PeMg-initiated PVC's whose $^{13}C\{^1H\}$ NMR spectra contained unassigned weak signals in the cyclopropane region.

The effects of polymerization temperature revealed in Figures 8 and 9, considered in conjunction with the attendant changes in polymer structure, show that two types of chain-growth termination were occurring in our systems. Low temperature favors quasiionic termination reactions that are mediated by magnesium. Below ca. 20 °C, these terminations are faster than free-radical transfer to monomer, and the molecular weight data show that their composite activation energy is less than that for propagation. Low conversion in this temperature region could result from slow initiation, fast termination, and destruction of the initiators in side reactions (see eq 19) that do not beget chains. When the temperature is increased, the initiators have an increasing tendency to undergo Mg−C homolysis in order to generate alkyl radicals.[27] These species can

start a free-radical polymerization whose occurrence is demonstrated by characteristic structural changes and by the well-known inverse effect of temperature on PVC molecular weight. That effect now becomes predominant, because chain growth now is limited mainly by transfer to VC, and because the activation energy of that process is higher than the activation energy for free-radical propagation.[23] The rather large polydispersity values (3.0−6.4) that are derivable from data in Table 1 signify the contemporaneous occurrence of the various reactions that curtail growth, each of which yields polymer chains with a distinctive average length.

Conclusions

The polymerization of VC initiated by di-*tert*-alkylmagnesium etherates yields polymers with alkene and cyclopropane ends that have no precedents in ordinary PVC. The formation of these structures can be rationalized, for the most part, with recourse to the well-known chemistry of organomagnesium compounds. Magnesium-mediated reactions that produce the unusual end groups are favored by low temperature and tend to become less important than conventional radical reactions when the temperature is raised.

Experimental Section

General. All manipulations of organomagnesium complexes were carried out under an atmosphere of prepurified argon or nitrogen, using standard Schlenk or dry-box techniques. Experiments involving other air- and moisture-sensitive substances also were performed under argon. Solvents were dried, if necessary, by conventional methods and then degassed just before use. In preparative experiments, product yields ordinarily were not determined, as the objective here simply was to obtain enough material for spectroscopic characterization.

The following materials were obtained from the indicated commercial sources and were used as received: *t*-BuLi (Aldrich), PhLi (Aldrich), *t*-BuMgCl (Aldrich), *t*-PeMgCl (Aldrich), Bu_3SnH (Aldrich), CuCl (Aldrich), $ZnCl_2$ (Aldrich), Zn dust (Aldrich), CH_2I_2 (Aldrich), *n*-octanal (Aldrich), 2,2-dimethylpropanal (Aldrich), 1-iodo-2,2-dimethylpropane (Aldrich), 1-nonene (Aldrich), 2-methyl-2-octene (Wiley), ethylene (nominal purity, 99.5+%, Aldrich), ethylene-d_4 (nominal isotopic purity, 98%, Cambridge), isobutene (Research grade, Matheson), Ph_3P (Strem), 1-bromooctane (Eastman), and azobis(isobutyronitrile) (AIBN, Pfaltz & Bauer). "Neohexene" (3,3-dimethyl-1-butene, Aldrich) was dried over 4A molecular sieves and degassed just prior to use. Vinyl chloride (Dow) was passed in succession through a 3A molecular sieve column and an Oxisorb P column (from MG Industries) and then stored in stainless steel containers. The commerical PVC specimen contained no additives and had number- and weight-average molecular weights of 2.8×10^4 and 5.8×10^4, respectively.

Instrumental Analysis. The ^{1}H NMR spectra were recorded by Bruker AMX-500 and AM-200 spectrometers operating at 500.14 and 200.13 MHz, respectively. In order to obtain the ^{1}H spectra of polymer samples, a 66° pulse and a repetition rate of 5 s were used. The $^{13}C\{^1H\}$ NMR spectra were obtained with the AMX-500 instrument at 125.77 MHz, using a 60° pulse angle and a pulse repetition time of 10 s. Both the ^{1}H and the ^{13}C spectra were referenced to internal Me_4Si (δ 0.00 ppm). For both types of NMR spectra, reduced PVC was examined in 1,2,4-trichlorobenzene (TCB)/*p*-dioxane-d_8 solutions (ca. 5:1 v/v) at 100 °C, and unreduced PVC was observed in THF-d_8 solutions at 50 °C. The ^{31}P NMR spectrum was recorded with the AM-200 spectrometer at 80.96 MHz and was referenced to external H_3PO_4 (δ 0.00 ppm).

Samples for GC analysis were taken from the polymerization head space with an automatic sampling valve leading to a chromatograph (HP5890 Series II) that was equipped with a Porapak QS packed column [80 in. × 0.125 in. (i.d.), 80/100 mesh]. The following GC conditions were used: injector, 100 °C; detector (FID), 250 °C; oven, 150 °C (isothermal, 11 min); carrier gas, helium (20 mL/min). Peaks were identified by comparing their retention times with those of authentic specimens.

The GPC samples were run at 40 °C as ca. 0.5% solutions in THF (sample size, 100 μL), using a PL gel column (3x mixed-bed B + 100 Å columns in series), THF (stabilized with 250 ppm of BHT) as the mobile phase (1.5 mL/min), and a Waters 410 refractometer detector. Molecular weights are reported in polystyrene equivalents.

Polymerizations. In a typical run, vinyl chloride (270 g) was charged into a 500-mL stainless steel reactor that then was equilibrated under nitrogen at the desired temperature. The polymerization was initiated by injection of a solution of the initiator in "isooctane" (2,2,4-trimethylpentane, 20 mL) and terminated by addition of methanol. After removal of the excess vinyl chloride by venting, the polymer was stirred overnight in methanol, recovered by filtration, and dried thoroughly at 50 °C under vacuum. Copolymerizations were conducted in an identical manner. The NMR spectra of the reductively dechlorinated polymers (see below) showed that chain transfer to isooctane was negligible under the conditions that were used.

Synthesis of Di-*tert*-butylmagnesium. A dry 200-mL Kjeldahl flask was charged with *t*-BuMgCl solution (2.0 M in ether, 40 mL, 80 mmol). The solution was cooled to 0 °C and combined with a solution of *t*-BuLi (1.7 M in pentane, 47.1 mL, 80 mmol) that was added during 15 min with stirring. Stirring was continued for an additional 30 min while the mixture was allowed to warm to room temperature. The mixture then was subjected to centrifugation, and the resulting clear, pale yellow solution was decanted from the residual LiCl. Solvent was removed from the solution *in vacuo* to give $(t\text{-Bu})_2Mg{\cdot}2Et_2O$ as a waxy, very pale yellow solid. (If a considerable additional amount of LiCl precipitated during the evacuation, the centrifugation was repeated.) The structure of the product was established by its ^{1}H NMR spectrum (200.13 MHz, benzene-d_6): δ 3.29 (q, CH_2 of Et_2O), 1.39 (s, CH_3 of *t*-Bu), and 0.83 ppm (t, CH_3 of Et_2O).

Synthesis of *tert*-Butyl-*tert*-pentylmagnesium. A dry 200-mL Kjeldahl flask was charged with 100 mL (100 mmol) of *t*-PeMgCl solution (1.0 M in ether), and the solution was cooled to 0 °C. A solution of *t*-BuLi (1.7 M in pentane, 59 mL, 100 mmol) then was added during 15 min with stirring. Stirring was continued for 1 h at 0 °C and for an additional hour at room temperature. Following removal of the volatiles under vacuum, the mixture was slurried in isooctane and centrifuged to obtain a yellow solution that was decanted from the solid residue of LiCl. Removal of isooctane from the solution *in vacuo* yielded *t*-Bu-*t*-PeMg·1.4Et_2O as a slightly viscous yellow liquid: ^{1}H NMR (500.14 MHz, toluene-d_8, 50 °C) δ 3.30 (q, CH_2 of Et_2O), 1.41 (br q, CH_2 of *t*-Pe), 1.25 (s, CH_3 of *t*-Bu), 1.23 (s, CH_3 of *t*-Pe), 1.11 (br t, CH_3 of *t*-Pe), and 0.95 ppm (t, CH_3 of Et_2O).

Reaction of PVC with Zinc. Following the procedure of Cais and Spencer,[7] a mixture of PVC (commercial sample, 9.12 g, 146 mmol of VC units), $ZnCl_2$ (0.17 g, 1.2 mmol), Zn dust (60.0 g, 918 mg-atom), and *p*-dioxane (750 mL) was subjected to reflux under argon for 7 h. The mixture then was cooled to just below the boiling point and filtered with suction to remove excess Zn. After cooling to room temperature, the filtrate was added with stirring to a large excess of methanol in order to precipitate the polymer, which was recovered by suction filtration, washed thoroughly on the filter with fresh methanol, and dried overnight at 50 °C under vacuum.

Reduction of PVC with Tri-*n*-butyltin Hydride. According to a well-established procedure,[1a,8,28] a solution of PVC (2.03 g, 32.5 mmol of VC units), Bu_3SnH (11.2 g, 38.5 mmol), and AIBN (0.048 g, 0.29 mmol) in THF (165 mL) was allowed to reflux with stirring overnight. After cooling, methanol was added in increments, with stirring, until precipitation of the polymer apparently was complete. The polymer was recovered by suction filtration. It then was extracted overnight with methanol in a Soxhlet apparatus, dried thoroughly *in vacuo*,

and subjected to a further overnight reduction at 94 °C with 1.78 g of Bu_3SnH and 0.019 g of AIBN in 125 mL of anhydrous xylenes. Following the addition of 0.89 g of Bu_3SnH and 0.010 g of AIBN, the reduction was continued at 94 °C for another overnight period. Addition of the cooled mixture to a large excess of methanol, with stirring, caused precipitation of the polymer, which was recovered by suction filtration, subjected to Soxhlet extraction with methanol overnight, and then dried at 50 °C under vacuum.

Cyclopropanation of 1-Nonene. A mixture of Zn dust (6.73 g, 103 mg-atom), anhydrous CuCl (10.2 g, 103 mmol), and ether (50 mL) was stirred and heated under reflux for 30 min. 1-Nonene (5.0 g, 40 mmol) and CH_2I_2 (13.9 g, 52 mmol) then were added in succession, and the mixture was heated under reflux for an additional 6 h while stirring was continued. Cooling and subsequent evaporation of the ether at room temperature during 60 h left a residue comprised of a red-brown precipitate and a liquid. Analysis of the liquid by ^{1}H NMR showed that it consisted of unchanged 1-nonene (12 mol %) and *n*-heptylcyclopropane (**5**, 88 mol %): ^{1}H NMR (500.14 MHz, $CDCl_3$) δ 0.64 (m, 1H, methine), 0.38 (m, 2H, ring methylene), and 0.01 ppm (m, 2H, ring methylene); ^{13}C{^{1}H} NMR [125.77 MHz, TCB/*p*-dioxane-d_8 (5:1 v/v), 100 °C] δ 34.95 (1C, *C*H_2 α to ring), 32.15, 29.78, 29.75, 29.58, 22.89, 14.05, 11.24 (1C, methine), and 4.72 ppm (2C, ring *C*H_2's).

Cyclopropanation of 2-Methyl-2-octene. The general procedure and order of addition were the same as those of the preceding experiment, and the following amounts of materials were used: Zn dust, 2.86 g (43.7 mg-atom); anhydrous CuCl, 3.91 g (39.5 mmol); ether, 20 mL; 2-methyl-2-octene, 1.85 g (14.7 mmol); CH_2I_2, 5.08 g (19.0 mmol). After 24 h of refluxing, the final mixture was allowed to stand at room temperature for an additional 24 h. The supernatant liquid then was separated by decantation, washed twice with fresh portions of saturated ammonium chloride solution, and dried over anhydrous magnesium sulfate. Removal of the ether on a rotary evaporator afforded a liquid residue that was shown by ^{1}H NMR analysis to consist of unchanged 2-methyl-2-octene (ca. 40 mol %) and 1,1-dimethyl-2-*n*-pentylcyclopropane (**6**, ca. 60 mol %): ^{1}H NMR (500.14 MHz, $CDCl_3$) δ 0.96 (s, 3H, ring C*H*$_3$ substituent), 0.95 (s, 3H, ring C*H*$_3$ substituent), 0.34 (m, 1H, methine), 0.25 (d of d, 1H, ring methylene), and −0.25 ppm (d of d, 1H, ring methylene); ^{13}C{^{1}H} NMR [125.77 MHz, TCB/*p*-dioxane-d_8 (5:1 v/v), 97 °C] δ 27.71 (1C, *trans*-*C*H$_3$), 25.48 (1C, methine), 20.42 (1C, ring *C*H$_2$), and 20.02 ppm (1C, *cis*-*C*H$_3$).

Synthesis of 2,2-Dimethyl-3-undecene (7). Method A. A stirred mixture of triphenylphosphine (29.0 g, 111 mmol) and 1-bromooctane (30.0 g, 155 mmol) was kept at ca. 100 °C overnight. The resultant yellow liquid solidified upon cooling to room temperature, but addition of an equal volume of toluene, followed by warming, produced two liquid layers. After decantation of the toluene solution, the other layer was washed by decantation with two fresh portions of warm toluene and then with an additional portion of toluene in a separatory funnel. Removal of toluene from the residual layer *in vacuo* gave a sticky yellow solid that was shown to be *n*-octyltriphenylphosphonium bromide by ^{1}H NMR analysis (500.14 MHz, $CDCl_3$): δ 8.00−7.40 (m, 15H, 3C$_6$*H*$_5$), 3.52 (br s, 2H, C*H*$_2$P$^+$), 1.48 (br s, 4H, 2C*H*$_2$), 1.05 (br s, 8H, 4C*H*$_2$), and 0.68 ppm (br s, 3H, C*H*$_3$).

A solution of PhLi (1.8 M in cyclohexane/ether, 28.9 mL, 52 mmol) was added with stirring to *n*-octyltriphenylphosphonium bromide (23.8 g, 52.3 mmol) and ether (75 mL), and the mixture was heated under reflux for 3.5 h. Cooling to room temperature, followed by the gradual addition of 2,2-dimethylpropanal (4.48 g, 52.0 mmol) to the orange solution, led to a vigorous reaction. When the addition was complete, the resultant solution (now dark red-brown) was heated under reflux for 3 h and then allowed to stand for 60 h at ambient temperature. The supernatant ether solution was separated by decantation, and the residual solid was extracted thoroughly with ether. Combination of the ethereal fractions, followed by concentration on a rotary evaporator and subsequent fractional distillation, gave a colorless liquid (bp ca. 100 °C at ca. 5 Torr) that was shown by its ^{1}H NMR spectrum to be a 16:84 mixture of the trans- and cis-isomers, respectively, of 2,2-dimethyl-3-undecene (**7**): ^{1}H NMR (500.14 MHz, benzene-d_6), trans, δ 5.53 (d of t, 1H, =C*H*), 5.41 (d of t, 1H, =C*H*), 2.03 (d of q, 2H, =CHC*H*$_2$), 1.35 (m, 10H, 5C*H*$_2$), 1.04 [s, 9H, (C*H*$_3$)$_3$C], and 0.90 ppm (t, 3H, C*H*$_3$CH$_2$); cis, δ 5.42 (d of t, 1H, =C*H*), 5.27 (d of t, 1H, =C*H*), 2.20 (d of q, 2H, =CHC*H*$_2$), 1.25 (m, 10H, 5C*H*$_2$), 1.14 [s, 9H, (C*H*$_3$)$_3$C], and 0.90 ppm (t, 3H, C*H*$_3$CH$_2$); ^{13}C{^{1}H} NMR [125.77 MHz, TCB/*p*-dioxane-d_8 (5:1 v/v), 100 °C], trans, δ 141.9 (1C, =*C*H-*t*-Bu), 125.3 (1C, =*C*HCH$_2$), 32.92 (1C, CHCH$_2$), 30.14 [3C, (*C*H$_3$)$_3$C], and 14.10 ppm (1C, *C*H$_3$CH$_2$); cis, δ 140.0 (1C, =*C*H-*t*-Bu), 129.2 (1C, =*C*HCH$_2$), 31.39 [3C, (*C*H$_3$)$_3$C], 28.73 (1C, =CH*C*H$_2$), and 14.10 ppm (1C, CH$_2$*C*H$_3$). Supporting evidence for the shift assignments was obtained from a 2D ^{1}H−^{13}C HETCOR experiment and from the vicinal coupling constants found for the alkene protons:[13] J_{HH} (trans) = 15.5 Hz; J_{HH} (cis) = 11.9 Hz.

Method B.[29] A mixture of triphenylphosphine (7.86 g, 30.0 mmol) and 1-iodo-2,2-dimethylpropane (9.00 g, 45.4 mmol) was stirred and heated under reflux for 6 h and then poured into ethyl acetate (300 mL). The resulting precipitate was recovered by suction filtration, washed on the filter with fresh solvent, air-dried, and recrystallized subsequently from chloroform−ethyl acetate at −20 °C to obtain neopentyltriphenylphosphonium iodide as white crystals: ^{1}H NMR (500.14 MHz, $CDCl_3$) δ 8.02 (m, 6H, phenyl groups), 7.71 (m, 9H, phenyl groups), 3.89 (d, 2H, C*H*$_2$-*t*-Bu), and 1.00 ppm [s, 9H, (C*H*$_3$)$_3$C]; ^{31}P{^{1}H} NMR (80.96 MHz, $CDCl_3$) δ 20.07 ppm (s). A mixture of the phosphonium iodide (7.0 g, 15 mmol) and ether (100 mL) was stirred while a solution of PhLi (1.8 M in cyclohexane−ether, 8.3 mL, 15 mmol) was added. The resultant mixture, which now was orange, was stirred for an additional 30 min at room temperature and then treated with *n*-octanal (1.92 g, 15.0 mmol) and heated under reflux with stirring overnight. Following a workup procedure which was similar to that of Method A (*vide supra*), **7** was isolated by fractional distillation under vacuum as a 27:63 trans:cis mixture, according to analysis by ^{1}H NMR.

Cyclopropanation of 2,2-Dimethyl-3-undecene (7). The procedure and order of addition were the same as those of the other cyclopropanations described above. Materials used were Zn dust, 1.96 g (30.0 mg-atom); anhydrous CuCl, 2.97 g (30.0 mmol); ether, 30 mL; **7** (trans:cis = 16:84), 2.20 g (12.1 mmol); and CH_2I_2, 4.04 g (15.1 mmol). The final mixture was subjected to 24 h of refluxing and then allowed to cool to ambient temperature. After its separation by decantation, the ether solution was washed with saturated ammonium chloride solution, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. Analysis of the liquid residue by ^{1}H NMR revealed the presence of ca. 70 mol % of unchanged **7** and 30 mol % of 1-*t*-butyl-2-*n*-heptylcyclopropane (**8**, trans:cis = 25:75): ^{1}H NMR (500.14 MHz, $CDCl_3$) δ 0.87 [s, *cis*-C(C*H*$_3$)$_3$], 0.74 [s, *trans*-C(C*H*$_3$)$_3$], 0.60−0.40 (m, 3H, H on ring C's), and −0.15 ppm (d of t, 1H, H on ring C); ^{13}C{^{1}H} NMR [125.77 MHz, TCB/*p*-dioxane-d_8 (5:1 v/v), 100 °C] δ 34.99 (*trans*-*C*H$_2$ α to ring), 30.50 [*cis*-C(*C*H$_3$)$_3$], 28.72 [*trans*-*t*-Bu*C*H], 28.68 [*trans*-C(*C*H$_3$)$_3$], 18.20 (*cis*-*n*-C$_7$H$_{15}$*C*H), 14.87 (*trans*-*n*-C$_7$H$_{15}$*C*H), 8.15 (trans ring *C*H$_2$), and 7.45 ppm (cis ring *C*H$_2$).

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