of the copolymer structure indicate that all the 1,4-cyclohexane units in the polymer chain are linked in a trans configuration. Therefore, it is concluded that in the copolymerization of 1 with 2 initiated by BF_3, the ring opening of 1 proceeds entirely with inversion of configuration, thus suggesting that in the propagation rate-determining step, the active species of 1 is in the form of a cyclic oxonium ion.

No search was made for cyclic oligomers or for structural irregularities (e.g., methyl branches) in the polymers in connection with a possible formation of carbenium ions from monomer 2. Recently, the presence of methyl groups in cyclization products obtained in the homo- and copolymerization of 1,2-epoxides has been reported as a convincing argument in favor of the carbenium nature of the growing species involved in these systems.[4]

Exhaustive discussion of the reactivity ratios r_1 and r_2 in terms of a copolymerization equation without a detailed knowledge of the formation of oligomers and other possible side reactions would be difficult.

Considering the process to consist essentially of four propagation steps, one can observe that when an active species of 2 is at the chain end, it apparently prefers to react with monomer 1 about 9 times faster than with another 2 monomer, as indicated by the value $r_2 = 0.11$.

Monomer 2 is a Lewis base weaker than other saturated and less strained cyclic ethers, according to the order[22] four- > five- > six- > three-membered ring while the basic strength of 1 is intermediate between that of oxetane (four-membered) and tetrahydrofuran[22] (five-membered).

Let us assume the basicity to be parallel to the monomer reactivity as nucleophile and suppose the nucleophilicity to be in this case a dominant factor. The lower basicity of 2 would therefore result in a lower reactivity than expected from its ring strain in the competitive reaction with 1. The value 0.66 for r_1 indicates that when the propagation reaction involves the oxonium ion 5, monomer 1, in spite of its higher basicity, appears to react with 5 about 1.5 times more slowly than monomer 2. This reverse trend of reactivity might be mainly due to steric effects. An increase of steric hindrance (in comparison with the addition of 2) would be expected by the hydrogens of the hydrocarbon cage partially surrounding the oxygen atom in 1 when this monomer and its own oxonium species 5 are approaching each other to form the corresponding transition state.

Steric hindrance, in addition to the reactivity of the monomer and the propagating species, plays an important role in governing the rate constant of S_N2 propagation reactions.[21,23] Unfortunately, the lack of the relevant activation parameters does not allow us to proceed further in considering the formulated hypothesis.

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Cationic Copolymers of Isobutylene. 6. NMR Investigation of the Structure and Sequence Distribution of Isobutylene–2,3-Dimethylbutadiene Copolymers

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ABSTRACT: The cationic copolymerization of isobutylene (I) with 1,3-dimethylbutadiene (DB), performed homogeneously at −70 °C, was investigated by studying the structure of the resulting copolymer (I–DB). Spectroscopic investigations, carried out mainly by ^1H and ^{13}C NMR, on the copolymer as well as on the cationic and anionic DB homopolymers, showed that the enchainment of DB in I–DB is trans-1,4. The complete interpretation of the ^{13}C NMR spectra of I–DB permitted us to calculate the distribution of the monomeric units, which indicated that I–DB shows a tendency toward a block-type structure.

Introduction

In previous papers we have investigated the structure of cationic copolymers of isobutylene (I) with butadiene[1] and its methyl derivatives, i.e., isoprene[2] and *cis*- and *trans*-1,3-pentadiene.[3,4] Pursuing our work, we have examined the I copolymers with some dimethyl derivatives

Table I
Copolymerization of Isobutylene (I) and 2,3-Dimethylbutadiene (DB)[a]

run no.	feed comp, mol fract of DB	conversion, %	copolymer comp,[b] mol fract of DB	$\bar{M}_n$
1	0.24	31	0.18	8500
2	0.28	43	0.24	9600
3	0.33	8	0.30	nd
4	0.42	20	0.32	7300
5	0.52	3	0.41	nd

[a] Experimental conditions: solvent = 1/1 (v/v) *n*-pentane + CH_2Cl_2; [I] + [DB] = 0.30 mol/L; T = −70 °C; [$C_2H_5AlCl_2$] = 0.015–0.025 mol/L; time = 15 min.
[b] Determined by ^{1}H NMR analysis.

of butadiene. The aim of this study is the investigation of the influence of two methyl groups on the reactivity of conjugated dienes in cationic copolymerization. Both electronic and steric effects are expected to arise from the presence of methyls on the diene system and to exert their influence on the stability and reactivity of the resulting carbenium ions. Actually, the structure of isobutylene–1,3-pentadiene copolymers was found to depend on the type of diene isomer involved.[3,4]

Recently, the relative reactivity of various dimethylbutadienes in cationic polymerization and the structure of the resulting polymers were investigated.[5] The prevalent repeat unit of the diene in these polymers was trans-1,4, even though some dienes yielded high amounts of cyclized units.

As far as the copolymerization of I with dimethylbutadienes is concerned, only the system I–DB (DB = 2,3-dimethylbutadiene) was preliminarily investigated, with BF_3 as initiator at −103 °C.[6] The study of this copolymer began with NMR spectroscopy, as in previous papers.[1-4]

Experimental Part

Reagents. Isobutylene, solvents, and $C_2H_5AlCl_2$ were purified and employed as described previously.[1] 2,3-Dimethylbutadiene (DB, Fluka, purity >99% by GCA) was distilled in vacuo before use and stored under dry nitrogen at 0 °C.

Procedure. The copolymerization runs were carried out as reported elsewhere,[1] using a mixture of *n*-pentane and CH_2Cl_2 (1:1 by volume) as solvent in order to guarantee a completely homogeneous system. Specific data concerning the experimental conditions and the results obtained are reported in Table I. DB was also homopolymerized anionically in order to obtain a model for ^{13}C NMR analysis (conditions: solvent = toluene, T = 50 °C, catalyst = *n*-BuLi (0.2 mmol/L), DB = 3.6 mol/L, time = 2 h, conversion = 55%).

The hydrogenation of the copolymers investigated was carried out as described previously.[1]

The GPC analysis of typical I–DB copolymer samples revealed a symmetrical unimodal distribution of molecular weight, in agreement with a homogeneous structure of the samples. Also the DTA analysis showed the presence of a single T_g whose value varied with the composition of the sample.

Analyses. The determination of molecular weight ($\bar{M}_n$) and GPC analyses were carried out as reported previously.[1] DTA investigations were performed with a DuPont instrument (Model 990). Both ^{1}H and ^{13}C NMR spectra were obtained as described in a previous paper.[2]

Results and Discussion

Structural Analysis. In analogy with previous papers,[1-4] the structural analysis of isobutylene–2,3-dimethylbutadiene copolymer (I–DB) was carried out by NMR, and Figure 1 shows a ^{1}H NMR spectrum of it. The interpretation of the spectrum is possible on the basis of an almost complete 1,4-enchainment of the diene unit, thus confirming literature reports on cationic DB homopolymers.[5] In fact, the olefinic region of the spectrum, between 4.5 and 5.5 ppm from Me_4Si, does not show any trace of signals attributable to vinylidene protons (CH_2=) resulting from the possible 1,2-unit. Therefore all the double bonds of I–DB are tetrasubstituted. IR analysis agrees with this conclusion on the basis of the absence of the band at 11.2 μm due to vinylidene unsaturation.

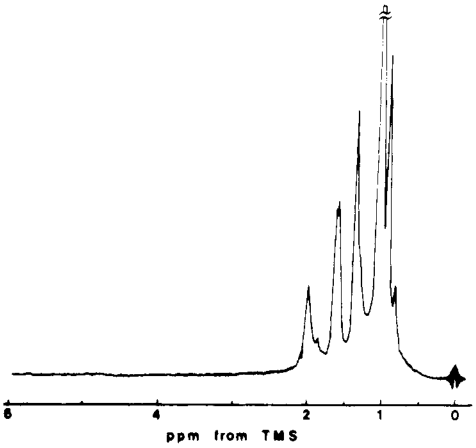


Figure 1. ^{1}H NMR spectrum of a cationic I–DB copolymer.

The spectrum of Figure 1 permits the calculation of the copolymer composition on the basis of the ratio between the areas of signals at 1.98 and 1.60 ppm (due to the methylenes and methyls of DB, respectively) and those of the upfield signals (between 1.4 and 0.8 ppm) due the protons of I. Also evident are upfield shifts (from 1.1 to 0.9–0.8 ppm) of the signals of I methyls in the triads III, IID + DII, and DID. By using the information obtained from ^{1}H NMR spectroscopy, we have completely interpreted the ^{13}C NMR spectra, yielding a thorough knowledge of the I–DB structure.

The revelant data collected in previous work[1-4] on the additive contribution of the *gem*-dimethyl group in ^{13}C NMR spectra allowed an easy interpretation of the I–DB spectrum. Only one region, that of the quaternary carbons of I, appears complex because of the overlapping of various signals, the assignments of which are not reported. However, the complete interpretation of the remainder of the spectrum has permitted us to obtain essentially complete information on the distribution of the monomeric units.

The ^{13}C NMR spectrum of the same I–DB sample of Figure 1 is shown in Figure 2A,B, which show the olefinic and aliphatic regions, respectively. The starting point for the interpretation of the spectrum was the assignment of signals of the DB carbons in the triad DDD. The peaks at 128.43, 33.32, and 18.10 ppm from Me_4Si correspond to unsaturated carbons, methylenes, and methyls of DB, respectively. The assignment is based on the comparison of the spectrum of DB homopolymer, obtained under the same conditions adopted for synthesizing I–DB, which shows three strong peaks corresponding to the resonances indicated above.

In the DB homopolymer spectrum there are also weak signals and, moreover, a trace of a broad band in the aliphatic region, typical of cyclized structures.[7] However, the three strongest peaks mentioned above indicate that the trans-1,4 structure is prevalent in the diene units. In fact, no signals of appreciable intensity are evident in the regions around 110 and 150 ppm from Me_4Si, where the resonances of unsaturated carbons belonging to a possible 1,2 unit are expected. The assignment of the trans configuration to the double bond of the 1,4-DB unit is based on literature data.[8] These literature data show that the

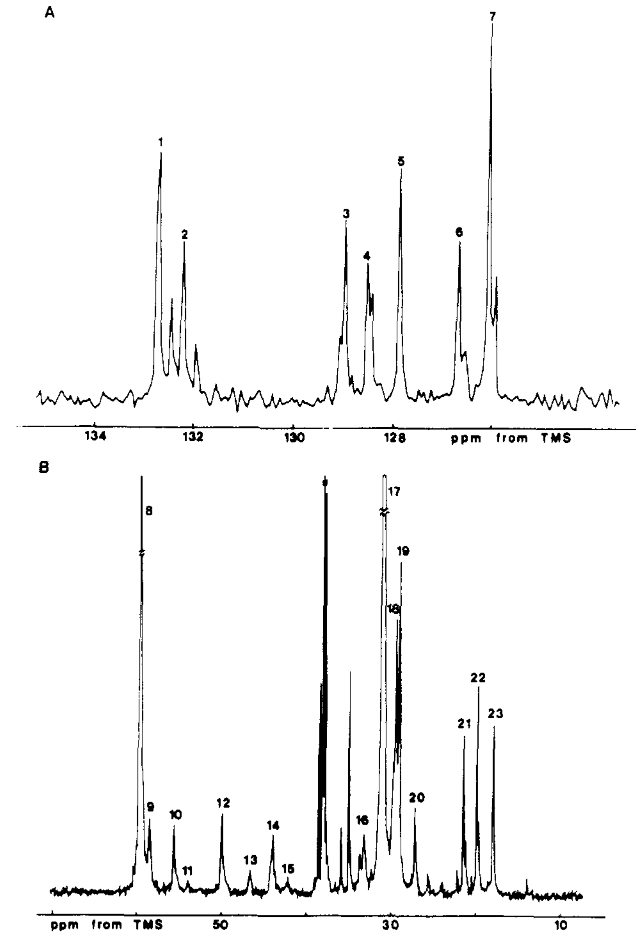
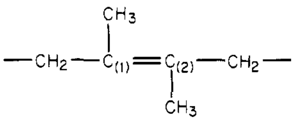


Figure 2. ^{13}C NMR spectrum of a cationic I–DB copolymer: (A) olefinic region; (B) aliphatic region.

Table II
^{13}C NMR Chemical Shifts (ppm) of the I-DB Copolymer: Olefinic Region

carbon	sequence	peak	chem shift	substitution
C(2)	IDI	1	132.65-132.36	$\nu' + \delta$
	IDD	2	132.12-131.85	ν'
	DDI	3	128.97-128.88	δ
	DDD	4	128.43	
C(1)	DDD	4	128.43	
	DDI	5	127.77	δ'
	IDD	6	126.60-126.49	ν
	IDI	7	126.00-125.85	$\nu + \delta'$

simultaneous presence of trans- and cis-1,4 units should give two resolvable methyl bands, two unsaturated carbon bands, and four methylene bands. Our spectrum of cationic poly-DB shows only one strong band in each of these three regions, and this means that only one configuration of the double bond is largely prevalent. As reported by Cantow et al.,[8] the chemical shift difference of corresponding carbon atoms in cis and trans configurations is quite small, so the configuration present in our cationically polymerized DB could not be determined from a direct comparison of chemical shifts of this polymer with published values for cis and trans structures. We therefore synthesized a sample of poly-DB with an anionic initiator (see Experimental Part). Comparison of the ^{13}C NMR spectrum of this polymer with published and assigned spectra of Cantow et al. showed that this sample contained all three possible structures of DB, i.e., 1,2, trans-1,4, and cis-1,4 units. The ^{13}C NMR spectrum of the anionically polymerized sample was then obtained under the same conditions used for obtaining the spectrum of cationic poly-DB. Comparison of these two spectra clearly showed that the cationic polymer had the trans configuration. The spectrum of I–DB copolymer was thus interpreted on the basis of trans-1,4 enchainment of the diene. The assignments of the olefinic region of the spectrum are reported in Table II. The notation $C_{(1)}$ and $C_{(2)}$ refers to the two unsaturated carbons of DB present in the chains as the unit



$$-CH_2-\overset{CH_3}{\overset{|}{C_{(1)}}}=\underset{\underset{CH_3}{|}}{C_{(2)}}-CH_2-$$

while I units arise from head-to-tail addition ($-CH_2C(CH_3)_2-$). In a similar fashion, we indicate the two methylenes as $CH_{2(1)}$ and $CH_{2(2)}$ and likewise for the methyls.

The assignments were carried out following the method adopted for the isobutylene–butadiene copolymer.[1] The resonance of the two unsaturated carbons of the DDD triad occurs at 128.43 ppm. The substitution of the neighboring diene units with I induces a downfield shift of the $C_{(2)}$ resonance while that of $C_{(1)}$ is shifted upfield. On the basis of the hypothesis put forward previously,[1] i.e., $\gamma' > \delta$ and $|\gamma| > |\delta'|$, the assignments shown in Table I can be calculated. The signals are, sometimes, split because of long-range effects (of type ϵ and ϵ' and of the order 0.1–0.2 ppm) arising from the second neighboring unit. As in the previous investigations,[1-4] the olefinic region permits the calculation of the values of the triad fractions centered on the diene (see below).

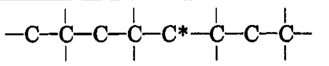
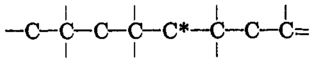
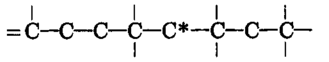
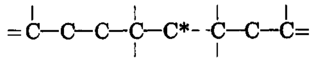
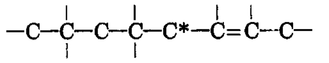
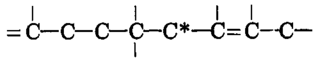
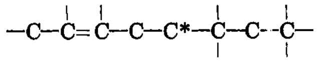
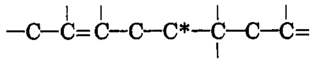
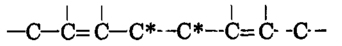
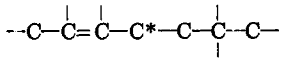
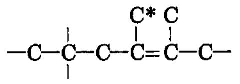
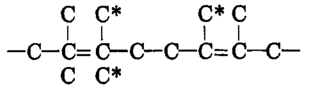
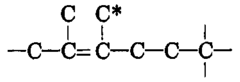
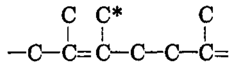
The assignments pertaining to the aliphatic part of the spectrum are reported in the Table III. The downfield region (60–40 ppm) is entirely occupied by methylene signals. The unique peaks of the CH_2 groups occurring upfield are at 33.32 ppm (DD sequence) and at 29.58 ppm. The assignments of methylene signals have been carried out, as in previous papers,[1-4] on the basis of selective decoupling experiments which allow one to distinguish the signals of CH_2 in the α position to the double bond from those of I methylene. In this way six peaks are attributable to the methylene of I (peaks 8, 9, 10, 11, 14, and 15) and four peaks are due to the methylenes of DB (peaks 12, 13, 16, and 18).

The complete assignment of all these signals can be easily obtained by referring to the spectrum of isobutylene–isoprene (I_B–I_P) copolymer[2] and taking into account the presence of a second methyl ($CH_{3(2)}$) in DB. Peaks 8, 9, 10, and 11 are attributed to the CH_2 group of I in tetrads IIII, IIID, DIII, and DIID, respectively, the chemical shift being practically coincident with that of the analogous tetrad of the I_B–I_P copolymer. Peaks 14 and 15, attributed to tetrads >DII and >DID (the symbol > means that the unit can be D or I), are shifted upfield by ca. 2 ppm with respect to the corresponding signals of the I_BI_P copolymer because of the γ contribution (negative) of the second methyl of DB.

For the signals in the α position to the double bond, peak 16 is due, as indicated above, to the methylenes of the four tetrads centered on the DD dyad. When we consider the tetrads centered on the DI dyad, the signal of the second methylene of DB, i.e., $CH_{2(2)}$, is shifted upfield because of the presence in the γ position of a *gem*-dimethyl group. This shift (3.74 ppm) is essentially analogous to that of the corresponding CH_2 of isoprene in the I_B–I_P copolymer, i.e., 26.92–23.23 ppm upon going from I_PI_P to I_PI_B.

Signals 12 and 13, attributed to $CH_{2(1)}$ of DB, are conversely shifted downfield relative to the peak at 33.32 ppm since the *gem*-dimethyl group is present in position $\beta + \delta$ and β, respectively. The resulting shifts are 16.52 and

Table III
^{13}C NMR Chemical Shifts (ppm) of the I-DB Copolymer: Aliphatic Region

carbon	structure	sequence	peak	chem shift
CH_2	 $-C-C-C-C-C^{*}-C-C-C-$	IIII	8	59.56
	 $-C-C-C-C-C^{*}-C-C-C=$	IIID	9	58.42
	 $=C-C-C-C-C^{*}-C-C-C-$	DIII	10	55.50
	 $=C-C-C-C-C^{*}-C-C-C=$	DIID	11	54.00
	 $-C-C-C-C-C^{*}-C=C-C-$	IID<	12	49.84
	 $=C-C-C-C-C^{*}-C=C-C-$	DID<	13	46.49
	 $-C-C=C-C-C^{*}-C-C-C-$	>DII	14	43.90
	 $-C-C=C-C-C^{*}-C-C-C=$	>DID	15	42.20
	 $-C-C=C-C^{*}-C^{*}-C=C-C-$	>DD<	16	33.32
	 $-C-C=C-C^{*}-C-C-C-$	>DI<	18	29.58
CH_3(I)		III	17	31.27
		IID + DII	19	29.19
		DID	20	27.26
CH_3(D) (1)	 $-C-C-C-C=C-C-$	ID<	21	21.62 21.32
	 $-C-C=C-C-C-C=C-C-$	DD<	23	18.10
CH_3(D) (2)	 $-C-C=C-C-C-C-$	>DI	22	20.00 19.79
	 $-C-C=C-C-C-C=$	>DD	23	18.10

13.17 ppm.

A comparison with the spectrum of the I_B–I_P copolymer largely confirms these assignments. In fact, the resonance at 39.69 ppm of the corresponding CH_2 in the tetrads centered on the I_PI_P dyad is shifted 15.90 ppm downfield for the tetrads $I_BI_BI_P$< and 11.96 ppm downfield for the tetrads $I_PI_BI_P$<.

Assignments completely analogous to those proposed in previous papers[1-3] are obtainable for the methyl of I in the four triads. For the DB methyls there is a downfield shift of ca. 1.9 ppm with respect to the resonance of the triad DDD because of an ϵ effect due to the *gem*-dimethyl group and a δ effect (3.5 ppm) of the same group.

Distribution of the Monomeric Units. By taking into account the assignments reported above, it is possible to calculate the triad and tetrad fractions. The values of the fractions of the triads centered on DB are directly obtainable, as indicated above, from the measurement of the areas of signals due to unsaturated carbons.

The fractions of the triads centered on I could be obtained from the areas of the peaks of the methyls belonging to this monomeric unit. However, the presence of a partial overlapping of peaks 19 (methyl of triads DII + IID) and 18 (methylenes of DB) gives rise to some inaccuracy in the measurement. Therefore, the values of these triad fractions have been obtained from the ^{1}H NMR spectra and by taking into account also in this case the peaks of I methyls.

For the tetrad fractions we have utilized the signals of the methylenes present in the ^{13}C NMR spectra. The relationship between signal number and sequence is as follows: peak 8, IIII; peak 9, DIII; peak 10, IIID; peak 11, DIID; peak 12, (IIDI + IIDD); peak 13, (DIDI + DIDD); peak 14, (IDII + DDII); peak 15, (IDID + DDID); $^1/_2$ peak 16, (IDDI + DDDI + IDDD + DDDD). Only half of peak 16 is considered since the resonance of two methylenes of the dyad DD is involved in it.

Table IV
Sequence Fractions in the I-DB Copolymer[a]

	triads			tetrads	
	exptl	calcd		exptl	calcd
III	0.831	0.672	IIII	0.555	0.452
IID + DII	0.147	0.296	DIII	0.087	0.099
			IIID	0.075	0.099
DID	0.022	0.032	DIID	0.017	0.022
IDI	0.443	0.672	IID<	0.097	0.121
DDI	0.219	0.148	DID<	0.026	0.027
IDD	0.230	0.148	>DII	0.087	0.121
DDD	0.108	0.032	>DID	0.028	0.027
			>DD<	0.028	0.032

[a] Sample no. 1 of Table I.

The values of the sequence fractions are reported in Tables IV and V for two copolymer samples and are compared with the values calculated for a random distribution. It is apparent that observed concentrations of homosequences are greater than the concentrations calculated for a random distribution. The reverse situation occurs when the alternate sequences are considered. The difference between experimental and calculated values is particularly

Table V
Sequence Fractions in the I-DB Copolymer[a]

	triads			tetrads	
	exptl	calcd		exptl	calcd
III	0.726	0.352	IIII	0.234	0.124
IID + DII	0.221	0.482	DIII	0.079	0.085
DID	0.053	0.166	IIID	0.063	0.085
IDI	0.210	0.352	DIID	0.024	0.058
DDI	0.235	0.241	IID<	0.113	0.143
IDD	0.267	0.241	DID<	0.091	0.098
DDD	0.288	0.166	>DII	0.102	0.143
			>DID	0.080	0.098
			>DD<	0.214	0.166

[a] Sample no. 5 of Table I.

evident in the case of the triad IDI. Therefore the I-DB copolymer displays a distribution of the monomeric units which is indicative of a tendency toward blockiness.

Conclusions

The spectroscopic analyses (IR and NMR) of cationic I-DB copolymers have shown that the enchainment of the diene is essentially trans-1,4. Signals attributable to other possible structural units of DB are not evident. The quantitative evaluation of the monomer sequence distribution indicates that I-DB shows the tendency to a block-type structure.

An analogous situation was found for isobutylene-butadiene copolymers.[1] But in that case the copolymerization system is more complex because the diene gives rise to different structural units and shows a great difference of reactivity relative to the olefin.[9] Conversely, I and DB exhibit a small difference of reactivity and hence the conclusions obtained concerning the copolymer structure surely reflect also the course of the copolymerization process. On the basis of the structural data obtained in this work, the product of the reactivity ratios of I and DB should be higher than one. Preferential solvation effects exerted by the monomers on the active centers[1] might explain these findings.

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50.3-MHz ^{13}C NMR Study of Chlorinated Poly(vinyl chloride) Microstructure and the Mechanism of Chlorination

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ABSTRACT: Carbon-13 NMR at 50.3 MHz has been used to study the microstructures of a series of solution-chlorinated PVC's (CPVC) in the earliest stages of the reaction (57-62% Cl) and the microstructure of a commercial CPVC (66% Cl). Resonances due to configurational isomers in sequences containing three adjacent CHCl carbons were observed for lightly chlorinated PVC and for a low molecular weight copolymer of vinyl chloride and 1,2-dichloroethylene. Configuration assignments were made on the basis of low molecular weight model compounds. At chlorine levels up to about 57.7% Cl only substitution at CH_2 carbons could be observed. However, CCl_2 carbons of isolated vinylidene chloride units were observed soon afterward ($\sim$58.3% Cl) in the product. This suggests that these structures were formed by a direct free-radical substitution mechanism rather than by a combined elimination-addition mechanism. Peak assignments for the commercial CPVC were made on the basis of calculated chemical shifts and the observed shifts of lightly chlorinated PVC and model copolymers. Results of spin-lattice relaxation experiments indicate that the chlorinated structures have restricted segmental mobility compared to PVC.

Introduction

The molecular structure of chlorinated poly(vinyl chloride) (CPVC) has been the subject of investigation for some time.[1,2] Although CPVC is simple in its basic composition, consisting predominantly of CCl_2, CHCl, and CH_2 groups, the many possible arrangements of these groups produce a very complex macromolecule. Both sequence distribution and CHCl configuration (in both the unchlorinated and chlorinated regions) must be taken into account to describe the microstructure of the polymer backbone.

The most powerful method available for characterizing the molecular structure of CPVC is nuclear magnetic resonance (NMR), particularly ^{13}C NMR. The sensitivity of the ^{13}C chemical shift to comonomer sequence distribution and tacticity makes it the method of choice for studying the microstructure of CPVC. The ability to directly observe CCl_2 carbons is a major advantage over ^{1}H NMR for CPVC. Unfortunately, the structural complexity of the polymers and the unfavorable NMR properties for CCl_2 carbons made the acquisition of high signal-to-noise ^{13}C spectra very difficult with the equipment available prior to the introduction of wide-bore, cryomagnet NMR systems.

We have prepared a series of CPVC's with very low degrees of chlorination and have examined the series using a cryomagnet-based, wide-bore NMR spectrometer operating at 50.3 MHz for ^{13}C. The relatively simple spectra, compared to that for commercial CPVC, facilitated some peak assignments and the observation of configurational isomers in the chlorinated segments. Identification of the first structures to appear during chlorination of PVC

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