(27) Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; Wiley-Interscience: New York, 1972; p 364.

(28) The differences in the magnitudes of the ^{13}C chemical shifts observed and calculated for methine and methylene carbons in the H–H:T–T and H–T structures may stem from the slightly different β substituents[23] present in each of these structural environments. Methine and methylene carbons in both H–H:T–T and H–T structures are β to oxygen ($CHCH_2O$ and CH_2CHO) and the methylene carbons are beta to methyl carbons (CH_2CHCH_3). However, H–T methine and H–H:T–T methylene carbons are β to methylene carbons ($CHOCH_2$ and CH_2OCH_2), while H–T methylene and H–H:T–T methine carbons are β to methine carbons (CH_2OCH and CHOCH) (see Table I). On the other hand, H–H:T–T and H–T methyl carbons have precisely the same α and β substituents. The fact that the calculated and observed methyl chemical shifts agree so closely lends support to the suggestion that slightly different β substituents for H–H:T–T and H–T methine and methylene carbons may be the source of the disparity between the magnitudes of their observed and calculated ^{13}C chemical shifts.

^{13}C NMR Studies of Sequence Distributions in Polymers Having All Rings in the Backbone: 1-Substituted 1,3-Poly(bicyclobutanes)

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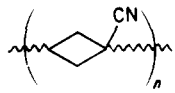
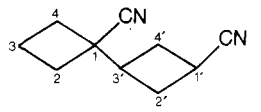
ABSTRACT: To better understand the stereochemistry of the class of unusual polymers having all 1,3-fused cyclobutane rings in the backbone, we obtained ^{13}C NMR results for poly(bicyclobutane-1-carbonitrile) (PBBC), poly(1-(methoxycarbonyl)bicyclobutane) (PMCB), poly(bicyclobutane-1-carboxamide) (PBCA), and some related oligomers. Using chemical shift data for trimers related to PBBC and PMCB, it was possible to assign all of the ^{13}C NMR resonances of the polymers. Triad sequences are observed in the –CN, COO–, and $-CONH_2$ resonances as well as for certain ring carbons in all three polymers. In contrast to vinyl and related polymers, there is a directionality in these polymer sequences that leads to additional multiplicity in the *n*-ad sequences. The quaternary carbons in PBBC and PMCB also exhibit pentad sequences, which are consistent with either Bernoulli or first-order Markov statistics within the experimental error. The ratio of trans/cis ring fusions are similar: 0.68:0.32, 0.66:0.34, and 0.73:0.27 for free radical initiated PBBC, PMCB, and PBCA, respectively.

In a previous NMR study[1] of polymers composed entirely of 1,3-fused cyclobutane rings in the backbone,[2-4] it was shown that the ^{13}C NMR spectrum of poly(bicyclobutane-1-carbonitrile) (PBBC) could be interpreted on the

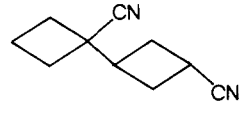


PBBC

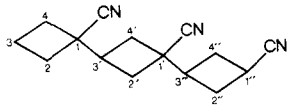
basis of studies of related model compounds. Of particular importance were the NMR spectra of many 3-substituted cyclobutane-1-carbonitriles, which included the two dimers [*cis*- and *trans*-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile, **1a** and **1b**] as well as the four trimers **2a–d**.



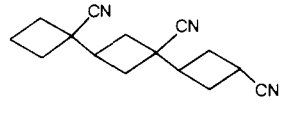
1a (*t*)



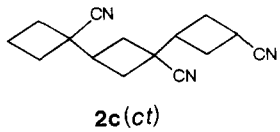
1b (*c*)



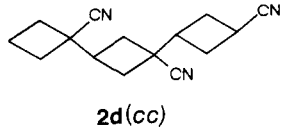
2a (*tt*)



2b (*tc*)



2c (*ct*)

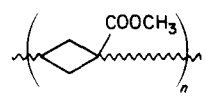


2d (*cc*)

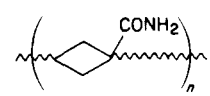
In all of the molecules studied substituents at C3, which were cis to the nitrile, led to nitrile ^{13}C NMR shifts that were 1–1.5 ppm upfield of the trans isomers. On this basis, it was concluded that the nitrile chemical shift provided a very useful probe of cis/trans stereochemistry in 3-substituted cyclobutane-1-carbonitriles as well as in PBBC. With notation of the trimers by the general form RR′R″, where the R's denote the 1-substituted cyclobutane moieties, it was suggested[1] that the ^{13}C NMR spectrum of PBBC arises as the superposition of resonances of the four R′ moieties of the trimers **2a–d**. From the ratios of the integrated intensities of the high-field and low-field CN resonances, for example, it was possible to infer the ratios of trans-to-cis ring enchainments depending on the method of initiation of polymerization.

The oligomers are given different designations than those used previously[1] to avoid confusion in the specification of the sequence distributions. In the present work cis (c) and trans (t) denote ring enchainments, and these are read from left to right. For example, the tc associated with the trimer (**2b**) RR′R″ (R denotes cyanocyclobutyl) implies that R and R″ are in a trans arrangement about R′ and that a cyanocyclobutyl group (R‴) must add in a cis fashion at C1″.

This work extends the previous ^{13}C NMR studies of PBBC to include the detailed assignments of both nitrile and ring carbon resonances and sequence determinations up to pentads. In fact, it will be shown that certain resonances, which were previously thought to be due to impurities,[1] arise because of pentad sequences in the ring carbons. Carbon-13 NMR studies of poly(1-(methoxycarbonyl)bicyclobutane) (PMCB) and related oligomers



PMCB



PBCA

provide an even better example for the appearance of triad and pentad sequences. Moreover, in the absence of all of the model compounds for poly(bicyclobutane-1-carbox-

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Table I
Carbon-13 NMR Chemical Shifts of PBBC Compared with Those of the Four Trimers and Fractions of Pentad, Triad and Diad Sequences

carbon C_i	δ(trimer),[a] ppm	sequence pentad/triad[b]	δ_i(PBBC), ppm	PBBC integrals[c]	fractional ring enchainment[d] pentad	triad	diad
CN	123.32 (123.12)[e]	ccc, tcc	122.95	0.31	(0.03), (0.07)	0.09 (0.10)	0.32
	123.11 (123.02)[e]	cct, tct	123.04	0.74	(0.07), (0.15)	0.23 (0.22)	
	121.93	ctc	121.79	0.26	0.08 (0.07)[f]		0.68
	121.79	ttc, ctt, ttt	121.66	1.96	(0.15), (0.15), (0.31)	0.60 (0.61)	
C1′	34.76	ccc, tcc	35.09	0.24		0.13 (0.10)	(0.32)[g]
	34.73	cct, tct	35.25	0.33		0.19 (0.22)	
	32.60	ctc, ttc	32.95	0.12	0.05 (0.07)	0.21 (0.22)	(0.68)[g]
			33.11	0.48	0.18 (0.15)		
	32.64	ctt, ttt	32.78	0.46	0.17 (0.15)	0.44 (0.46)	
			32.66	0.80	0.29 (0.31)		
C3′	34.01	cc	34.82	0.32		0.09 (0.10)	0.31 (0.32)
	33.94	ct	34.98	0.80		0.22 (0.22)	
	34.02	tc	33.59	0.62		0.17 (0.22)	0.68 (0.68)
	34.09	tt	33.80	1.84		0.51 (0.46)	
C2′, C4′	31.16	ccc, tcc	31.75	0.020		0.09 (0.10)	0.34 (0.32)
	31.25	cct, tct	31.47	0.019	0.09 (0.07)	0.25 (0.22)	
			31.63	0.035	0.16 (0.15)		
	31.10	ctc, ttc	30.82	0.056		0.26 (0.22)	0.66 (0.68)
	30.96	ctt, ttt	31.20	0.088		0.40 (0.46)	

[a] These values are given in ref 1. [b] The eight possible pentads are R R′R″R‴R⁗. [c] These are crude integrals taken directly from the computer output, values varied within about 5% in different spectra. These values were taken from a single spectrum of 100K transients collected into 16K, zero-filled into a 64K data table and resolution-enhanced by Gauss–Lorentz multiplication. The data for the C2′ and C4′ carbons were obtained under conditions of more extensive resolution enhancement. [d] It was assumed that the cis/trans ring fusions were in the ratio of 32% to 68% based on the results for the nitrile resonance. [e] In ref 1 both of these resonances occurred in the trimer; it was not possible to distinguish the one associated with the central cyclobutanecarbonitrile moiety. [f] See text for explanation. [g] The upfield and downfield integrals were individually normalized to 0.68 and 0.32, respectively.

amide) (PBCA), it was possible to use the triad structure of the carboxamide and quaternary carbons to investigate the stereochemistry of the polymer.

Results and Discussion

Poly(bicyclobutane-1-carbonitrile) (PBBC). The ^{13}C NMR spectrum of free radical initiated PBBC, which was recorded at 62.90 MHz in Me_2SO-d_6 solvent, is given in Figure 1a. The syntheses and spectral details are given in the Experimental Section. The expanded nitrile region (Figure 1c) consists of four clearly resolved resonances in this resolution-enhanced spectrum. In order to remove certain ambiguities in the overlapping methine and quaternary region, the pseudo-INEPT[5] or APT[6] spectrum was obtained (Figure 1b). The ^{13}C chemical shifts of PBBC are given in the fourth column of Table I for the four types of carbons specified in the first column. Also included in the second column of the table are the chemical shifts of the middle (R′) moieties for each of the four trimers **2a–d** from ref 1. Values in parentheses are given because of ambiguities in the assignments of the trimers.[1] There is good agreement between the trimer chemical shift data and the PBBC data. However, the recognition of pentad sequences in the C1′ carbons of PBBC removes certain ambiguities in the assignments of the spectrum of the polymer.

Also included in Table I are the relative peak areas or integrals associated with each of the PBBC resonances. These values are crude, uncorrected values taken from the computer output of a single spectrum. Results obtained by the "cut-and-weigh" method[7] agree with the computed fractions within at least 5%. Moreover, comparison of the fractions computed from different carbons in PBBC and

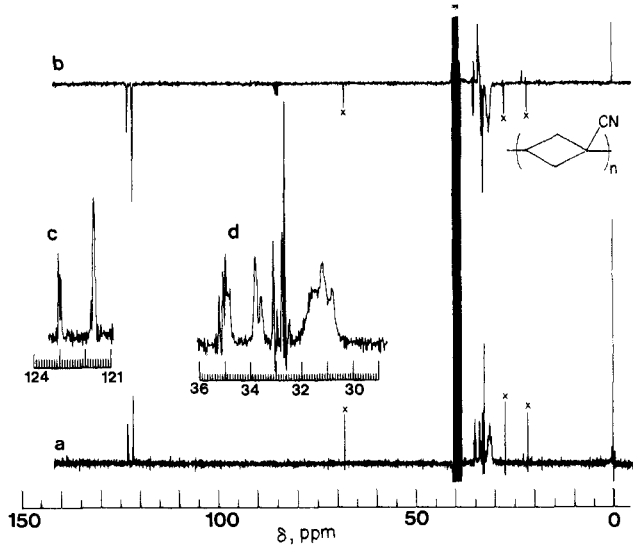


Figure 1. (a) 62.90-MHz ^{13}C NMR spectrum of free radical initiated poly(bicyclobutane-1-carbonitrile) in Me_2SO-d_6. (b) Pseudo-INEPT spectrum of the ring carbon resonances. (c) Expansion of the nitrile resonances. (d) Expansion of the ring carbon resonances. The scales below the spectra are in ppm downfield of internal Me_4Si. Impurities are designated with an x.

the other polymers of this study support this estimate of the accuracy of the integrals. For each type of carbon the fractional populations of the sequences were calculated by using Bernoulli trial statistics.[7-9] The methylene assignments and integrals were based on a spectrum with greater resolution enhancement.

In analogy to the terminology, which is used in studies of vinyl and related polymers,[7-9] the various ring enchainment sequences are designated diad, triad, and pentad. The nitrile resonances at highest field, which were previously assigned to trans-ring fusions (tt and tc triads), constitute about 68% of the total area. Therefore, the value of $P_t = 0.68$ was used to calculate the triad and pentad fractions assuming Bernoulli trial statistics.[7-9] These are given in parentheses in the columns labeled pentad, triad, and diad in Table I. The cis and trans content were obtained from the triad and pentad sequences by a slight modification of the necessary relationships,[7-9] wherein ct is distinguished from tc, etc. However, any nonequality of the fractions associated with these sequences is assumed to be due to the experimental error.

The (partial) pentad sequence for the quaternary (C1′) carbons of PBBC at δ 32.0 to 32.7 in Figure 1d and Table I can be identified by the similarity of the intensity ratios for the triads of C3′, for example. The results are consistent with Bernoulli trial values, which are in parentheses in Table I, within the estimated experimental error.

The nitrile resonance at 121.79 ppm in Figure 1c has a much lower integrated intensity than would be expected on the basis of the fraction of triad sequences; the tc and tt sequences are expected to have fractions 0.22 and 0.46, respectively, from Bernoulli trial values and the experimental results are 0.21 (0.17) and 0.44 (0.51) for C1′ (C3′), respectively, in Table I. Only six of the eight resonances for the quaternary (C1′) carbon appear in Figure 1d. However, the fraction (0.07%) of one of these sequences (ctc) is consistent with that observed (0.08%) for the apparently anomalous nitrile resonance at 121.79 ppm. Therefore, the resonance at highest field (about 60% of the nitriles) must comprise unresolved ttc, ctt, and ttt pentad sequences. The sum of the fractions for the C1′ diad sequences cc and ct in Table I was less than 32%. The reason for this is not clear; it could be due to the overlap with the resonances of C3′ or to some differential NOE. In order to make use of the data (cc + ct) and (tc + tt) diads were normalized to 0.32 and 0.68, respectively. As a consequence, the diad fractions given in parentheses in Table I are assumed values. A Bernoullian distribution appears to be consistent with the limited data available for PBBC.

Poly(1-(methoxycarbonyl)bicyclobutane) (PMCB) and Related Oligomers. The ^{13}C NMR spectrum of the free radical initiated PMCB, which was recorded at 62.90 MHz in Me_2SO-d_6 solvent, is given in Figure 2. The syntheses and experimental spectral details are given in the Experimental Section. Both the carbonyl and methine (C3′) carbons exhibit four resonances; the methoxy CH_3O– consists of two resonances and the (C1′) carbons give two bands, each having four resonances. The methylenes give a broad feature at highest field. Further understanding of the stereochemistry of PMCB was based on studies of model compounds that are rather loosely termed "monomers", dimers, trimers, etc. Obviously, the actual monomer is 1-(methoxycarbonyl)bicyclobutane. Entered in Table II are the ^{13}C chemical shifts of the "monomer" (methoxycarbonyl)cyclobutane **3** and the two dimers *cis*- and *trans*-3-(1-(methoxycarbonyl)cyclobutyl)-1-(methoxycarbonyl)cyclobutane **4a** and **4b**, respectively, measured in Me_2SO-d_6 solvent. Assignments are based on relative intensities, the attached proton test and additivity relationships.[10] Moreover, the dimers[4] and trimers **5a–d**, which serve as model compounds for PMCB, were obtained from the analogous nitriles of known stereochemistry.[1]

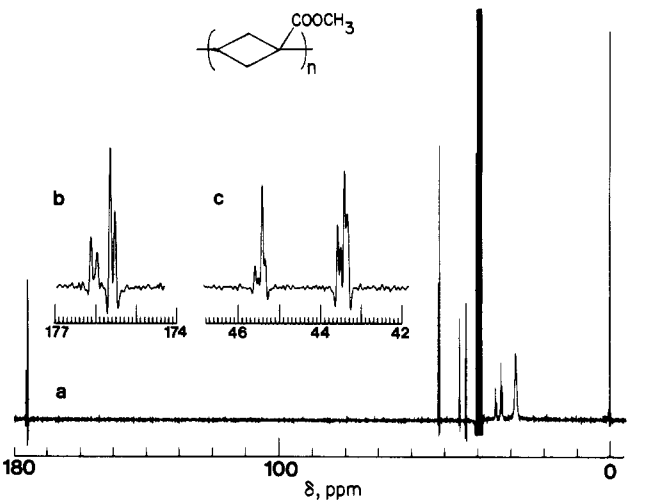
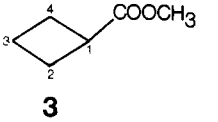


Figure 2. (a) 62.90-MHz ^{13}C NMR spectrum of free radical initiated poly(1-(methoxycarbonyl)bicyclobutane) in Me_2SO-d_6. (b) Expansion of the carboxyl resonances. (c) Expansion of the quaternary (C1′) resonances. The scales below the spectra are in ppm downfield of internal Me_4Si.

Table II
^{13}C NMR Chemical Shifts of (Methoxycarbonyl)cyclobutane 3 and the Cis and Trans Dimers 4a and 4b[a]

	3	4a	4b
δ_1	37.11	48.38	48.54
δ_2, δ_4	24.74	26.38[b]	25.95[b]
δ_3	17.82	14.83	14.83
δ_{COO^-}	174.92	176.11	176.25
$\delta_{CH_3^-}$	51.17	51.46[c]	51.42[c]
$\delta_{1'}$		35.45	37.00
$\delta_{2'}$, $\delta_{4'}$		25.62[b]	25.62[b]
$\delta_{3'}$		32.13	33.06
$\delta_{C'OO^-}$		174.46	175.58
$\delta_{C'H_3^-}$		51.29[c]	51.46[c]

[a] All values were measured in parts per million downfield of internal Me_4Si with Me_2SO-d_6 as solvent, digital resolution 0.03 ppm. [b] Values in this column could be interchanged. [c] Values for the methoxy resonances in this column could be interchanged.



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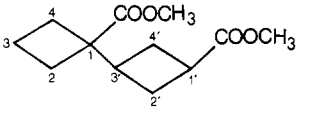
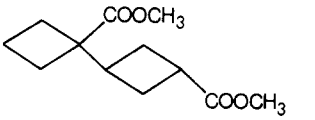


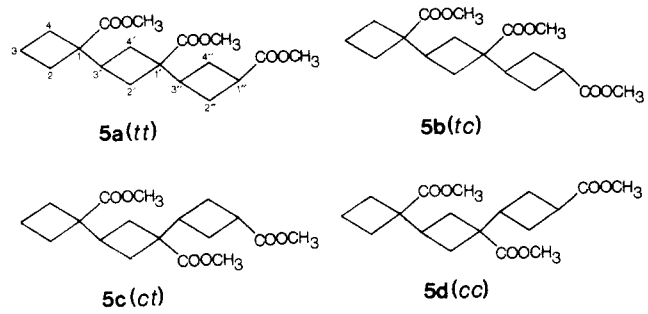
4a(t)



4b(c)

Key differences in the chemical shifts for the dimers in Table II occur for $\delta_{1'}$, $\delta_{3'}$, and $\delta_{C'O^-}$; values for the isomer **4a** are about 1.5, 1.0, and 1.1 ppm upfield of the isomer **4b**. These are analogous to the differences between the chemical shifts of these groups in the corresponding nitrile dimers and suggest by analogy that these resonances in the trimers offer potential for the determination of cis/trans stereochemistry in the polymer.

The experimental ^{13}C chemical shifts for the trimers **5a–c** were measured in Me_2SO-d_6 and the results are en-



tered in Table III. There was an insufficient quantity of **5d** for a ^{13}C NMR spectrum. For purposes of predictive value it was of interest to compare the experimental data with those obtained empirically from the "monomer" and dimer data in Table II. The changes $\Delta\delta_C$ in the chemical shifts, which occur on introducing the (methoxycarbonyl)cyclobutyl group at positions X, Y, and Z in the (methoxycarbonyl)cyclobutane moiety, were calculated and entered in Table IV. These substituent parameters were used in combination with the dimer data in Table II to calculate empirically the chemical shifts of the four trimers. These are entered along with the experimental data in Table III. The agreement between the experimental and the (empirically) calculated values for the chemical shifts of the carboxyl COO– groups is good; the average deviation being less than 0.2 ppm. Moreover, where the trimers **5a–d** are denoted by RR′R″ (R = (methoxycarbonyl)cyclobutyl), the agreement between the experimental and calculated values for the R and R″ ring carbons is also quite good and accounts for correlation coefficients of 0.9998 for the three sets of data. However, the correspondence between the experimental and calculated values for the R′ moieties is poor in contrast to the results for the nitrile trimers **2a–d**. This should not be a surprise because the methoxycarbonyl group is bulkier than the nitrile group; there is substantially more strain on the R′ ring, and, with the possible exception of **5d**, the methoxycarbonyl group on R′ will be twisted away from the C3–C1′–C(O) plane.

Space-filling models suggest that steric effects are more important for the trimers than the dimers, primarily because of the bulky methoxycarbonyl groups. The situation is similar to that found recently in studies of the ^{13}C NMR spectra of 17 electron-deficient olefins having nitrile and methoxycarbonyl substituents.[11] In addition to the substituent parameters $\Delta\delta_i$ (such as those in Table IV), an adequate correlation of the olefinic carbon resonances required the introduction of pairwise additive parameters. The latter appeared to be associated with geminal or cisoid methoxycarbonyl substituents, which are known[12] to produce deviations from planarity in olefinic systems.

It is of interest to compare the ^{13}C chemical shifts of the R′ moieties of the trimers with those that occur in the PMCB spectrum in Figure 2. The ^{13}C chemical shift data for the R′ ring of the trimers in Table III suggest that each type of carbon in PMCB could exhibit four resonances. Possible exceptions are the methyl and methylene groups, for which the chemical shift range is small. In Table V these data are compared with those for PMCB. Chemical shift results for **5d**, which were based only on empirical calculations, are included in parentheses in Table V. For the ring carbons these are in very poor correspondence, which further indicates the inadequacy of simple additivity of substituent parameters. However, the experimental trimer data from Table III agree quite well with those for the polymer in Figure 2 and in Table V. The carboxyl and C3′ carbons exhibit the expected four resonances; there are two unresolved methyl resonances and a broad reso-

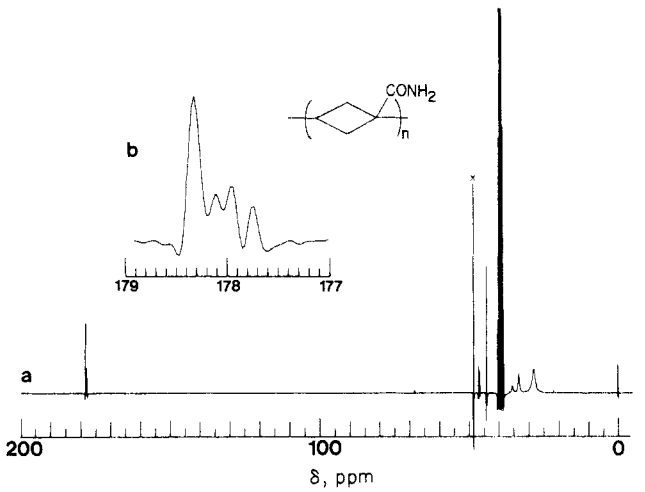


Figure 3. (a) 62.90-MHz ^{13}C NMR spectrum of free radical initiated poly(bicyclobutane-1-carboxamide) in Me_2SO-d_6. (b) The carboxamide resonances are expanded to exhibit the triad structure.

nance at about δ 28.4 from the methylene carbons. The C1′ quaternary carbons, however, exhibit two groups of four resonances, which are expanded in Figure 2c, and correspond to a complete pentad sequence (in contrast to PBBC).

Also included in Table V are the integrals associated with each of the PMCB resonances. For each type of carbon (except the methylenes) fractional populations of the sequences were calculated and are given in parentheses in the table. The integrals for the two methyl resonances of PMCB indicate that the fractions of cis and trans diad sequences are 0.34 and 0.66, respectively. If Bernoulli trial statistics are followed,[7-9] then the resulting fractions in the triad sequences should be 0.12, 0.22, 0.22, and 0.44 for cc, ct, tc, and tt triads, respectively. For the carboxyl and C3′ carbons, which exhibit four resonances, these fractions are 0.13–0.14, 0.18–0.23, 0.21–0.22, and 0.42–0.47, respectively. The recognition of the applicability of Bernoulli statistics removes several ambiguities in the assignments of the resonances associated with the cc and ct sequences.

The chemical shifts of the eight resonances, which arise for the quaternary (C1′) carbons of PMCB, are entered in Table V along with integrated intensities and the resulting fractions of each pentad sequence. The agreement with the Bernoulli trial results with $P_t = 0.66$, which are given in parentheses in Table V, is reasonable except for the disparity in the tct pentad sequence. In contrast to vinyl and related polymers,[7-9] the written direction of the polymer sequence is important; e.g., the ct sequence has a chemical shift that is different from tc. Because of different steric interactions in the growing polymer chain, it was of interest to investigate the applicability of first-order Markov statistics. Therefore, with the assumption that the probability of the monomer adding in a trans (cis) fashion to a cis (trans) chain end $P_{c,t}$ is 0.81 ($P_{t,c} = 0.31$) the fractions are compared with the experimental and Bernoulli trial sequence results in Table VI. The first-order Markov statistics give results within the estimated experimental error, but there is not yet sufficient data to say that these statistics are clearly obeyed.

The regularity of the changes in the chemical shift differences (0.08 ± 0.01 ppm) in the pentad sequence, for example, in Table VI suggests a common mechanism; i.e., a *cis*-1-(methoxycarbonyl)cyclobutyl group at the C1′′′′ position of an R′′′′ moiety in the sequence RR′R″R‴R′′′′ will lead to greater steric interactions with the 1‴-methoxycarbonyl function in the R‴ moiety than a *trans*-1-

Table III
Carbon-13 Chemical Shifts for the Four Trimers of PMBC[a]

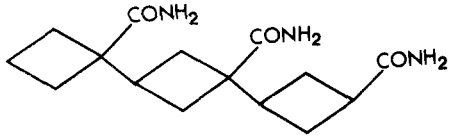
	5a		5b		5c		5d
	exptal	calcd	exptal	calcd	exptal	calcd	calcd
			R				
δ_1	48.53	48.38	48.53	48.38	48.64	48.54	48.54
δ_2, δ_4	26.62[b]	26.38	26.62[b]	26.38	26.41[b]	25.95	25.95
δ_3	14.76	14.83	14.76	14.83	14.84	14.83	14.83
δ_{COO^-}	176.24	176.11	176.24	176.11	176.11	176.25	176.25
$\delta_{CH_3^-}$	51.51[d]	51.46	51.51[d]	51.46	51.63[d]	51.42	51.42
			R′				
$\delta_{1'}$	43.40	46.72	43.46	46.88	45.30	48.27	48.43
$\delta_{2'}$, $\delta_{4'}$	27.97[b]	27.26	28.09[b]	26.83	27.80[b]	27.26	26.83
$\delta_{3'}$	32.79[c]	29.14	32.17[c]	29.14	34.38[c]	30.07	30.07
$\delta_{C'OO^-}$	175.61	175.65	175.78	175.79	176.26	176.77	176.91
$\delta_{C'H_3^-}$	51.51[d]	51.58	51.51[d]	51.52	51.81[d]	51.75	51.81
			R″				
$\delta_{1''}$	35.64	33.45	37.31	37.00	35.29	35.45	37.00
$\delta_{2''}$, $\delta_{4''}$	25.94[b]	25.62	25.82[b]	25.62	26.41[b]	25.62	25.62
$\delta_{3''}$	32.17[c]	32.13	33.05[c]	33.06	30.58[c]	32.13	33.06
$\delta_{C''OO^-}$	174.41	174.46	175.61	175.58	174.45	174.46	175.58
$\delta_{C''H_3^-}$	51.31[d]	51.29	51.51[d]	51.46	51.29[d]	51.29	51.46

[a] Chemical shifts are measured downfield of internal Me_4Si, Me_2SO-d_6 solvent, digital resolution 0.03 ppm. [b] The assignments of the methylene resonance of each isomer are ambiguous. [c] These assignments within a column may be reversed. [d] Within a given column the methoxy group resonance assignments are ambiguous, the only justification for this assignment is the correspondence with the polymer results in Table V.

(methoxycarbonyl)cyclobutyl group. Any resulting change in the pucker angle of the R‴ ring would lead to a small change in the (angularly dependent) γ effect at the C1″ position.

Poly(bicyclobutane-1-carboxamide) (PBCA) and Related Oligomers. Entered in Figure 3a is the ^{13}C NMR spectrum of PBCA, which was obtained under free radical conditions. The chemical shift patterns for PBCA in Figure 3a are similar to those for PMCB in Figure 2a. However, there is not as much structure; only three lines occur for the C1′ carbons and the two C3′ resonances are not resolved. There is an impurity (methanol) line at 48.4 ppm in Figure 3a. The four carboxamide resonances are expanded in Figure 3b.

Since the oligomers, which were associated with PBCA, were derived from the PBBC oligomers 1 and 2, their stereochemistry was known. In addition to the dimers, only one trimer, 6, was obtained in sufficient quantity for



6

the NMR parameters to be extracted (see Experimental Section). The procedures used for PMCB (vide supra) and PBBC,[1] wherein the ^{13}C chemical shifts of the central carbons were calculated from monomer and dimer data, led to results that were in very poor conformity with the experimental data for PBCA. Therefore, the approach adopted here was to make use of the similarities of the PMCB and PBCA spectra in Figures 2 and 3, respectively.

The ^{13}C chemical shifts of PBCA are given in the third column of Table VII. Also included are the integrals and fractions in the diad and triad sequences. Since the carboxamide resonances in Figure 3b cover a range of less than 0.6 ppm, in the absence of any other criteria, it would be exceedingly difficult to assign these to the four types of ring enchainments that occur for the trimers. However, in analogy to the data for PMCB in Table V, the C1′ and C3′ resonances each occur in two groups separated by about 2 ppm. In view of the similarities in the α, β, and γ substituent effects of the methoxycarbonyl and the carboxamide functional groups, it is reasonable to assign the high-field resonances to tc and tt triads. From the integrals for these two resonances, it is calculated that the fraction of trans-fused rings in the polymer is about 0.73. On the basis of values 73% trans, 27% cis diads, the Bernoulli trial values are 53%, 20%, 20%, and 7% for tt, tc, ct, and cc triad sequences, respectively, in reasonable conformity with the fractions for the carboxamide group in Table VII.

The occurrence of the carboxamide resonance for trans-ring fusions to low field of those for the cis-ring fusions was somewhat of a surprise since this is just opposite to that for the nitrile and methoxycarbonyl resonances. However, as noted previously,[1] the upfield shifts of the nitrile resonances on cis substitutions was not expected to be a general phenomena because it does not occur, for example, in the cases of methyl-substituted cyclobutanes.[13]

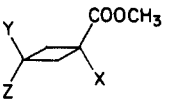
Conclusions

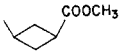
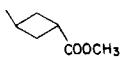
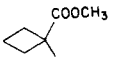
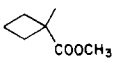
This NMR study of polymers having all cyclobutane rings in the backbone extends previous work on PBBC,[1] wherein it was shown that the integrated intensities of the PBBC nitrile resonances could be used to determine the ratio of cis-to-trans ring enchainments. It is now clear that the experimental ^{13}C chemical shift data for the R′ moieties of the four trimers RR′R″ are consistent with triad sequences that are observed in PBBC, PMCB, and PBCA. In addition, pentad structure is observed for the quaternary (C1′) carbons in PBBC and PMCB but not in PBCA. The observation of pentad structure provides a rationalization of several unexplained features in the PBBC spectrum. The pentad sequences in PMBC appear to be in better conformity with first-order Markov statistics than Bernoulli trial statistics, as might be expected in a situation in which steric effects involving the substituents are substantial.

Experimental Section

Spectra. All carbon-13 NMR spectra were obtained in 10-mm sample tubes at 62.90 MHz on a Bruker Instruments WM-250

Table IV
Changes in the Carbon-13 Chemical Shifts $\Delta\delta$ on Introducing (Methoxycarbonyl)cyclobutyl Substituents into the X, Y, and Z Positions of the (Methoxycarbonyl)cyclobutane Moiety[a]



X	Y	Z	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_3$	$\Delta\delta_{COO^-}$	$\Delta\delta_{CH_3^-}$
	H	H	11.27	1.64	−2.99	1.19	0.29
	H	H	11.43	1.21	−2.99	1.33	0.35
H		H	−1.66	0.88	14.31	−0.46	0.12
H	H		−0.11	0.88	15.24	0.66	0.29

[a] All values in ppm, Me_2SO-d_6 solvent.

Table V
Carbon-13 NMR Chemical Shifts of PMCB Compared with the Results for the Trimers and Fractions of Pentad, Triad, and Diad Sequences

carbon C_i	δ(trimer),[a] ppm	sequence pentad/triad	δ_i(PMCB), ppm	PMCB integrals[b]	fractional ring enchainment[c] pentad	triad	diad
C′OO	(176.91)	cc	175.96	0.29		0.14 (0.12)	0.32 (0.34)
	176.26	ct	176.09	0.36		0.18 (0.22)	
	175.78	tc	175.39	0.42		0.21 (0.22)	0.68 (0.66)
	175.61	tt	175.64	0.93		0.47 (0.44)	
C′H_3	(51.81)	cc	51.82	1.12			0.34
	51.81	ct					
	51.51	tc	51.47	2.13			0.66
	51.51	tt					
C1′	(45.43)	tcc	45.59	0.124	0.05 (0.08)	0.07 (0.12)	0.36 (0.34)
		ccc	45.50	0.045	0.02 (0.04)		
	45.30	tct	45.42	0.634	0.24 (0.15)	0.29 (0.22)	
		cct	45.34	0.127	0.05 (0.08)		
	43.46	ttc	43.58	0.320	0.12 (0.15)	0.20 (0.22)	0.65 (0.66)
		ctc	43.51	0.199	0.08 (0.08)		
	43.40	ttt	43.42	0.714	0.27 (0.29)	0.45 (0.44)	
		ctt	43.34	0.486	0.18 (0.15)		
C3′	(30.07)	cc	34.23	0.37		0.13 (0.12)	0.36 (0.34)
	34.38	ct	34.54	0.64		0.23 (0.22)	
	32.17	tc	32.44	0.60		0.22 (0.22)	0.64 (0.66)
	32.79	tt	32.88	1.16		0.43 (0.44)	
C2′, C4′	(26.83)	cc	~28.4				
	27.80	ct					
	27.97	tc					
	28.09	tt					

[a] Values from Table III. [b] See footnote *c* of Table I. [c] It was assumed that the cis/trans ratio was 0.34:0.66 based on the methyl group diad fraction.

Table VI
Bernoulli Trial and First-Order Markov Statistics Applied to the Quaternary (C1′) Carbon in PMCB

tetrad sequence	obsd[a]	Bernoulli[a] trial, P_t = 0.66	first-order Markov[b]
tcc	0.05	0.08	0.04
ccc	0.02	0.04	0.01
tct	0.24	0.15	0.18
cct	0.05	0.08	0.04
ttc	0.12	0.15	0.17
ctc	0.08	0.08	0.07
ttt	0.27	0.29	0.34
ctt	0.18	0.15	0.17

[a] Values from Table V. [b] Calculated with $P_{c,t}$ = 0.81 and $P_{t,c}$ = 0.31.

FT NMR spectrometer. Chemical shifts were measured in ppm downfield of internal tetramethylsilane (Me_4Si). Spectra of polymers were observed in Me_2SO-d_6 and some oligomers were

Table VII
Carbon-13 NMR Data for Poly(bicyclobutane-1-carboxamide)

carbon C_i	triad sequences	δ_i, ppm	PBCA integrals	fractional ring enchainment[a] triad	diad
C′ONH_2	cc	177.81	0.31	0.09 (0.07)	0.27
	ct	178.01	0.62	0.18 (0.20)	
	tc	178.17	0.61	0.18 (0.20)	0.73
	tt	178.38	1.87	0.55 (0.53)	
C1′	cc	46.83	0.49	0.13 (0.07)	0.29 (0.27)
	ct	46.48	0.62	0.16 (0.20)	
	tc, tt	44.12	2.78		0.71 (0.73)
C3′	cc, ct	35.40	1.10		0.27 (0.27)
	tc, tt	33.27	2.96		0.73 (0.73)
C2′, C4′	cc, ct, tc, tt	28.29[b]	6.32		

[a] On the basis of the results for the $CONH_2$ group, it was assumed that the trans/cis ring fusions were in the ratio 73% to 27%. Values in parentheses were calculated from these. [b] Broad, unresolved resonance.

studied in chloroform-*d*. Spectral widths of 15000 Hz were collected into 16K data tables. Resolution-enhancement techniques were applied to almost all spectra. In order to assign the oligomers and polymers, the attached proton test was used with $\tau = 0.0076$ s.

Syntheses. Routine proton spectra were obtained on a Varian Associates T-60 CW NMR spectrometer, infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer, and melting points were measured on a Thomas-Hoover apparatus and are uncorrected.

Monomers, Dimers, and Trimers of Bicyclobutane-1-carbonitrile. These compounds were synthesized and separated according to the reported method[1] with some modifications, which improved the yield.

Polymers. The reported free radical initiated polymerization conditions[14,15] were used to obtain poly(1-(methoxycarbonyl)bicyclobutane), poly(bicyclobutane-1-carboxamide), and poly(bicyclobutane-1-carbonitrile).

(Methoxycarbonyl)cyclobutane (3). Cyanocyclobutane (6 g) was dissolved in 20 mL of methanol, and 10 mL of concentrated sulfuric acid was added carefully. The mixture was heated under reflux for 16 h by using an oil bath adjusted to 80 °C. The mixture was poured into 200 g of crushed ice and extracted with 5 × 100 mL portions of ether. The ether solution was extracted with 2 × 100 mL portions of saturated sodium carbonate solution and then dried over $MgSO_4$ for 24 h. After filtration and evaporation of solvent, (methoxycarbonyl)cyclobutane was obtained as a clear liquid (5.43 g, 90%): ^{13}C NMR ($CDCl_3$) δ 18.55, 25.41, 38.12, 51.50, 175.90; IR (neat) 2953, 1735, 1172 cm^{-1}.

Dimers of (Methoxycarbonyl)cyclobutane (4a,b). The procedure that was used to prepare **3** was applied, starting with 120 mg of *cis*-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (**1a**). After the solvent was evaporated, the residue was purified by TLC, yielding 20 mg of *cis*-3-(1-(methoxycarbonyl)cyclobutyl)-1-(methoxycarbonyl)cyclobutane **4a** and 10 mg of *trans*-3-(1-(methoxycarbonyl)cyclobutyl)-1-(methoxycarbonyl)cyclobutane **4b**: ^{13}C NMR, see Table II; IR (Me_2SO-d_6), 1723 cm^{-1}.

Trimers of (Methoxycarbonyl)cyclobutane (5a–c). The trimer of cyclobutane-1-carbonitrile **2a** (100 mg) was converted to a mixture of the trimers of (methoxycarbonyl)cyclobutane **5a** and **5b** by the procedures used to prepare **3** and **4**. The trimers were purified by preparative TLC (eluted with 5:2 ratio benzene/chloroform) to yield 25 mg of a 2:1 ratio mixture of **5a** and **5b**: ^{13}C NMR spectra, see Table III.

A 4/1 mixture of the trimers **2b** and **2c** (130 mg) was converted to the methoxycarbonyl derivative by the procedures that were used to prepare **3** and **4**. The products were purified by preparative TLC, yielding 25 mg of a 3/1 mixture of **5b** and **5c**: see Table III for ^{13}C NMR data.

Cyclobutane-1-carboxamide. A 100-mL round-bottom flask was charged with 6.0 g of cyanocyclobutane, 6.7 g of H_2O, and 4.0 g of BF_3·2HOAC complex. The mixture was heated to 115–120 °C for 10 min and then cooled with ice water. Potassium hydroxide (6 N) was added carefully until the solution was basic. The mixture was extracted with 4 × 200 mL of 1:1 ethyl acetate/ether solution. The organic layer was dried with $MgSO_4$ and the solvent evaporated to give a white crystalline solid (5.37 g, 73%): mp 156 °C; ^{13}C NMR (Me_2SO-d_6), δ 17.66, 24.59, 38.47, 175.93; IR (KBr) 3362, 3182, 1632, 1426, 1296, 1136 cm^{-1}.

Dimers of Bicyclobutane-1-carboxamide. The procedure used to prepare cyclobutane-1-carboxamide was also used to obtain the dimers. (a) *cis*-3-(1-carbamylcyclobutyl)cyclobutane-1-carboxamide (25 mg): ^{13}C NMR (Me_2SO-d_6) δ 14.47, 26.14, 26.09, 33.48, 36.31, 49.28, 175.54, 178.15; IR (Me_2SO-d_6), 3374, 1664 cm^{-1}. (b) *trans*-3-(1-carbamylcyclobutyl)cyclobutane-1-carboxamide (~20 mg): ^{13}C NMR δ 14.58, 25.62, 26.37, 33.86, 37.67, 49.49, 176.86, 176.29; IR (Me_2SO-d_6), 3442, 1659 cm^{-1}.

Trimer of Bicyclobutane-1-carboxamide (5). Several attempts to obtain trimers of bicyclobutane-1-carboxamide by heating with water and BF_3·2HOAC complex led to an incomplete reaction or some side reactions. Therefore, basic hydrogen peroxide hydrolysis was used to obtain this trimer.

The trimer of bicyclobutane-1-carbonitrile (180 mg) was dissolved in 20 mL of 95% ethanol and 10 mL of 30% H_2O_2, and 10 mL of 6 N NaOH solution was added. The reaction was stirred at 50 °C for 4 h. After cooling to room temperature, the solution was neutralized with 8 M H_2SO_4. Then ethanol was removed with a rotary evaporator. The residue was extracted with 4 × 100 mL portions of 1:1 ethylacetate/ether solution. The organic layers were combined and dried over $MgSO_4$. After filtration and solvent removal, the residue was purified by TLC to obtain the trimer of bicyclobutane-1-carboxamide (20 mg): ^{13}C NMR (Me_2SO-d_6) δ 14.52, 25.96, 26.61, 28.05, 32.65, 33.03, 36.49, 43.91, 49.37, 175.82, 177.85, 178.35; IR (Me_2SO-d_6) 3643, 3269, 1662, 1623 cm^{-1}.

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Registry No. **1a**, 88315-87-1; **2a**, 88315-86-0; **2b**, 88336-04-3; **2c**, 88336-05-4; **3**, 765-85-5; **4a(t)**, 100928-90-3; **4b(c)**, 100928-91-4; **5a(tt)**, 100928-92-5; **5b(tc)**, 100992-55-0; **5c(ct)**, 100992-56-1; **5d(cc)**, 100992-57-2; **6**, 100928-93-6; PBBC, 25639-86-5; PBCA, 30472-59-4; PMCB, 30472-53-8; cyanocyclobutane, 4426-11-3; cyclobutane-1-carboxamide, 1503-98-6; *cis*-3-(1-carbamylcyclobutyl)cyclobutane-1-carboxamide, 100928-94-7; *trans*-3-(1-carbamylcyclobutyl)cyclobutane-1-carboxamide, 100928-95-8.

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