In addition, evidence for S–S annihilation was found for PPA, which further implies significant singlet energy migration. Moreover, all ester polymers were found to have photolabile side groups.

Acknowledgment. We acknowledge the financial support of the National Science Foundation (Grant DMR-8013709) and the Robert A. Welch Foundation (Grant F-356). We also acknowledge the help of the staff and the use of the facilities of the Center for Fast Kinetics Research, which is supported jointly by the Biotechnology Branch of the Division of Research Resources of the NIH (Grant RR00886) and the University of Texas at Austin. Special acknowledgment is made to Brent Hyman, who carried out much of the monomer synthesis and polymerization for PPA and PAMMA.

Registry No. I, 51960-29-3; II, 88315-88-2; III, 88315-89-3; methacryloyl chloride, 920-46-7; 9-anthrylmethyl 2-methylpropanoate, 88315-77-9; 9-anthracenemethanol, 1468-95-7; isobutyryl chloride, 79-30-1; 10-phenyl-9-anthrylmethanol, 24451-26-1; (10-phenyl-9-anthryl)methyl methacrylate, 85702-19-8; (10-phenyl-9-anthryl)methyl 2-methylpropanoate, 88315-78-0; 9-anthrylmethyl ethyl ether, 86170-50-5; bromoethane, 74-96-4.

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Nitrile Function as a Probe of Cis/Trans Stereochemistry: ^{13}C NMR Studies of Poly(bicyclobutane-1-carbonitrile) and Related Model Compounds

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ABSTRACT: To better understand the stereochemistry of poly(bicyclobutane-1-carbonitrile) (PBBC), ^{13}C NMR studies were performed for a series of 3-substituted cyclobutanes. Of particular interest were the syntheses and NMR assignments for the two dimers (*cis-* and *trans-*3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile) and the four trimers. In all of the molecules studied, substituents at C3, which were cis to the nitrile, led to ^{13}C NMR shifts of the nitrile that were 1–1.5 ppm to high field of those for the trans isomer; therefore the nitrile chemical shift is a very useful probe of cis/trans stereochemistry in cyclobutanecarbonitriles. Using data for cyclobutanecarbonitrile and the two dimers, we obtained additivity relationships; the calculated ^{13}C resonances of the four possible trimers are in very good agreement with the experimental values for the trimers. Furthermore, the shifts of the central cyclobutanecarbonitrile moieties of the four trimers are completely consistent with the nitrile resonances and account for most of the features of the ring carbon resonances of PBBC. As a consequence, the approximate 1:3 ratio of the intensities of the low-field to high-field CN resonances for the anionic-initiated PBBC indicates that about 75% of the rings are trans fused.

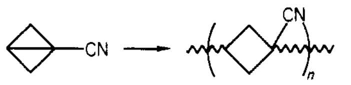
The stereochemistry of polymers based on vinyl and diene monomers and possessing all-carbon backbones have been extensively investigated by proton and ^{13}C NMR methods. It has been shown that bridgehead-substituted bicyclobutanes are a new family of highly reactive monomers which also yield polymers with all-carbon backbones upon polymerization.[1-3] These monomers polymerize by opening the bond between the C1–C3 bridge, yielding

Table I
Carbon-13 Chemical Shifts of a Series of Substituted Cyclobutanecarbonitriles[a]

compd	δ_1	δ_2	δ_3	δ_{CN}	δCH_3
1	22.86[b]	22.86[b]	22.86[b]		
2	22.16 [21.57 (6)]	27.23 [26.78 (6)]	19.95 [19.69 (6)]	122.47 [122.77 (6)]	
3	16.86 (6)	38.76 (6)	47.80 (6)	120.56 (6)	
4	18.94 (6)	37.80 (6)	50.66 (6)	121.50 (6)	
5	50.63	39.29	16.25	119.71	
6	12.99[c] (6) [12.41][c]	36.84[c] (6) [36.91][c]	63.23[c] (6) [62.65][c]	121.92[c] (6) [122.44][c]	
7	15.53[c] (6) [15.01 (6)]	38.02[c] (6) [38.08 (6)]	64.86[c] (6) [64.21 (6)]	123.22[c] (6) [123.67 (6)]	
8	24.43[c] (6)	43.86[c] (6)	62.45[c] (6)	124.91[c] (6)	22.29[c] (6)
9	25.86[c] (6)	44.58[c] (6)	61.35[c] (6)	125.49[c] (6)	22.29[c] (6)
10	26.87[b]	38.51[b]	26.87[b]		22.47[b]
11	26.10[b]	36.44[b]	26.10[b]		22.00[b]

[a] In parts per million downfield of internal tetramethylsilane with $CDCl_3$ as solvent; the values in parentheses are errors in the last figure cited. Chemical shifts in brackets were measured in Me_2SO-d_6. Unless noted otherwise, digital resolution was at least 0.03 ppm. [b] Reference 9. [c] These values were obtained in the mixture of the cis and trans isomers. The assignments were based on the different cis/trans ratios and the assumption that the nitrile resonances of the cis isomers are to high field of the trans isomer.

polymers composed entirely of cyclobutane rings in the backbone. In particular, bicyclobutane-1-carbonitrile readily undergoes polymerization by free radical or anionic-initiated conditions to give the high molecular weight polymer (PBBC) poly(bicyclobutane-1-carbonitrile) in high yield.



The geometry of the cyclobutane ring permits either 1,3-cis or 1,3-trans enchainment during polymerization. There have been no systematic studies performed of the structures present in these polymers. An attempt was made[4] to prepare a stereoregular PBBC using dialkylmagnesium and magnesium dialkylamide initiators; the ^{13}C NMR results described herein suggest that these polymers have a higher proportion of the trans-fused cyclobutanecarbonitrile rings.

To better understand the stereochemistry of polymers having the cyclobutane backbone, ^{13}C NMR studies were performed for the homopolymers, a series of substituted cyclobutanecarbonitriles, the two dimers, and four trimers of bicyclobutane-1-carbonitrile. Relatively little ^{13}C NMR data for substituted cyclobutanes have appeared. In a recent ^{13}C NMR study of methylated cyclobutanes and ethyl cyclobutanecarboxylates[5] the chemical shifts for cyclobutane were more accurately reported. Results for the ^{13}C NMR shifts of a series of 1-chloro- and 1-bromo-1-methylcyclobutanes,[6] cyclobutanecarbonitrile (**2**),[7] and the ring carbons of *cis*- and *trans*-3-chlorocyclobutanecarbonitrile (**3** and **4**)[8] have been reported.

Results and Discussion

^{13}C NMR of Poly(bicyclobutane-1-carbonitrile). The ^{13}C NMR spectrum of the anionic-initiated PBBC,[1,2] which was obtained at 37.73 MHz (in Me_2SO-d_6 as solvent) is shown in Figure 1. The nitrile region of the spectrum, which has been expanded in the figure, exhibits two major resonances at δ 121.71 (2) and 123.05 (2). The ratio of the area of the low-field to high-field resonances is 1:3.42. Additional structure in the two nitrile resonances was confirmed by examination of the nitrile region in a narrower spectral width at 62.90 MHz. Four peaks occur at δ 121.70 (2), 121.79 (2), 122.95 (2), and 123.05 (2) ppm.

The ^{13}C NMR spectrum of PBBC, which had been obtained under free radical conditions,[1,2] was measured in Me_2SO-d_6 at 22.63 MHz. In this case the ratio of the areas of the low- to high-field nitrile resonances was 1:1.8. It will be shown (vide infra) that the high-field CN resonances arise from fusions of the cyclobutanecarbonitrile moiety, which are cis to the nitrile; hence, the anionic initiation of the polymerization may lead to a slightly greater proportion of trans-fused cyclobutanecarbonitrile rings.

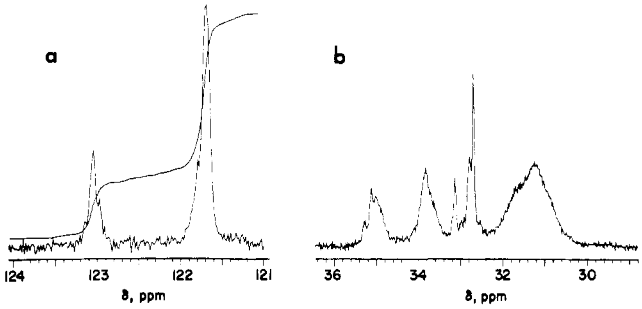
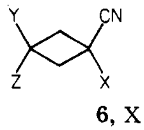


Figure 1. 37.73-MHz ^{13}C NMR spectra of the anionic-initiated poly(bicyclobutane-1-carbonitrile) (PBBC) in Me_2SO-d_6: (a) the nitrile region of the spectrum on the left has been expanded both vertically and horizontally; (b) the ring carbon region of PBBC. The scale at the bottom is in ppm from Me_4Si.

^{13}C NMR of Substituted Cyclobutanecarbonitriles. Entered in Table I are the ^{13}C chemical shifts for cyclobutane (**1**, representative cyclobutanecarbonitriles **2**–**9** (see



2, X = H; Y = H; Z = H
3, X = H; Y = Cl; Z = H
4, X = H; Y = H; Z = Cl
5, X = Cl, Y = H, Z = H
6, X = H; Y = OH; Z = H
7, X = H; Y = H; Z = OH
8, X = CH_3; Y = OH; Z = H
9, X = CH_3; Y = H; Z = OH

Experimental Section), and the *cis*- and *trans*-1,3-dimethylcyclobutanes (**10** and **11**, respectively). Shifts are measured in ppm downfield of Me_4Si in chloroform-*d* solvent. Values in brackets were measured in Me_2SO-d_6 solvent.

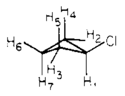
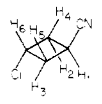
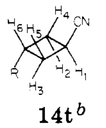
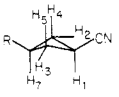
The assignments of cis/trans stereochemistry for the 3-chloro isomers **3** and **4** were based on infrared spectroscopic data.[8] Additional confirmation in these studies were based on the vicinal and long-range H–H coupling constants obtained by an iterative six-spin spectral simulation for **3**. Moreover, in the process of separating the two isomers it was found that the trans isomer was substantially more volatile than the cis, in conformity with the expected differences in the dipole moments. The two

Table II
Carbon-13 Chemical Shifts in Dimers of 3-(1-Cyanocyclobutyl)cyclobutanecarbonitrile (14c and 14t) and Their 1-Chloro Derivatives 15c and 15t[a]

compd	δ_1	δ_2, δ_4	δ_3	$\delta_{CN(C1)}$	$\delta_{1'}$	$\delta_{2'}, \delta_{4'}$	$\delta_{3'}$	$\delta_{CN(C1')}$
14c	17.25	29.21[b]	38.02	120.85	38.47	29.08[b]	16.41	122.73
	(16.05)	(28.66)[b]	(36.85)	(121.66)	(38.28)	(28.66)[b]	(16.05)	(122.90)
14t	18.46	28.46[b]	38.51	122.51[c]	38.93	29.86[b]	16.25	122.77[c]
	(17.68)	(27.49)[b]	(37.43)	(123.16)	(38.15)	(28.66)[b]	(15.86)	(123.16)
15c								
exptl[d]	46.92	40.78	36.03	118.03	38.16	29.54	16.41	122.09
calcd[e]	45.72	41.27	34.32	118.09	37.97	29.08	16.41	122.73
15t								
exptl[d]	45.10	41.85	34.83	119.64	38.74	29.79	16.41	122.09
calcd[e]	46.93	40.52	34.81	119.75	38.43	29.86	16.25	122.77

[a] In parts per million downfield from tetramethylsilane with $CDCl_3$ as solvent; digital resolution 0.03 ppm; values in parentheses were measured in Me_2SO-d_6 with a digital resolution of 0.06 ppm. [b] The chemical shift assignments of the C2 (C4) carbons may be interchanged with those for C2′ (C4′) in both the cis and trans isomers. [c] The assignments of the nitrile resonances in the trans isomer may be interchanged; this particular choice gives somewhat better correspondence between the calculated and experimental values for $\delta_{CN(C1)}$ in isomer **15t**. [d] The two isomers were not separated, the ^{13}C assignments were based on the cis/trans ratio of 62% **15c** and 38% **15t**. [e] These values were calculated empirically by using the data for dimers **14c** and **14t**, $\Delta\delta_C$ values from Table III, and the assumptions that carbon atoms in a position δ to a chlorine would be shielded by 0.5 Hz, and that carbon atoms further removed would not be affected.

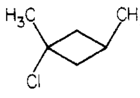
Table III
Proton Chemical Shifts (in ppm) and Coupling Constants J (in hertz) for Substituted Cyclobutanes

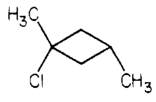
	 **16**[a]	 **4**	 **14t**[b]	 **14c**[b]
δ_1	4.32	3.36	3.25	3.22
$\delta_2 = \delta_3$	2.49	2.89		
$\delta_4 = \delta_5$	2.27	2.62		
δ_6	1.99	4.61	3.04	
δ_7	1.76			2.80
$J_{12} = J_{13}$	7.31	5.39	4.59	8.39
$J_{14} = J_{15}$	8.24	9.60	9.57	9.79
J_{16}	−0.90	−1.18	(−) 1.23	
J_{17}	0.11			<0.3
J_{23}	4.70	3.28		
$J_{24} = J_{35}$	−11.55	−12.74		
$J_{25} = J_{34}$	−1.02	−1.01		
$J_{26} = J_{36}$	2.98	7.40		
$J_{27} = J_{37}$	8.04			
J_{45}	0.47	2.07		
$J_{46} = J_{56}$	9.85	6.20		
$J_{47} = J_{57}$	9.87			
J_{67}	−10.99			
rms error	0.055	0.053		

[a] Reference 9. [b] R = cyanocyclobutyl.

isomer pairs **6**, **7** and **8**, **9** were not separated. The assignment for these were based on the following criteria: (1) of the seven isomer pairs that were examined, including the five reported in this study, the species occurring in greatest concentration in the mixture had its nitrile resonance 1–1.5 ppm upfield of the less abundant species. (2) In those cases in which the isomers were separated (**3** and **4**, the dimers, and the trimers to be discussed in subsequent sections) the cis isomers had the nitrile resonances 1–1.5 ppm to upfield of the trans isomer.

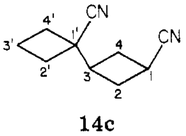
Data for the cis and trans isomers of 1,3-dimethylcyclobutane (**10** and **11**, respectively), which are also included in Table I, indicate that the methyl group resonance does not exhibit an analogous stereochemical dependence. Moreover, it is interesting to note that the C1-methyl group of **12** is 2.5 ppm to low field of the corresponding methyl group in **13**.[6] In analogy to δ-effects in rigid systems[9] it was proposed that this may be due to a contribution of the syn-diaxial conformation with equatorial chlorine.

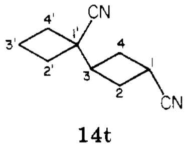

12

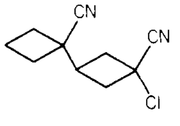

13

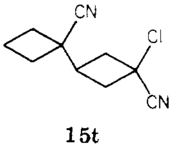
The upfield nitrile shift, which is noted for all of the cis-3-substituted compounds investigated here, appears to have a common origin which is independent of the ring conformation; possibly it arises from the removal of the nonbonded H···CN interaction on substitution of group Y at the C3 carbon.[10]

^{13}C NMR of the Dimers of 3-(1-cyanocyclobutyl)-cyclobutane-1-carbonitrile (14c and 14t) and 1-Chloro-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (15c and 15t). The syntheses and separation procedures for the dimer pairs (**14** and **15**) are described in the Experimental Section. The ^{13}C chemical shifts of the compounds dissolved in chloroform-d and Me_2SO-d_6 (values in parentheses) are entered in Table II. One of the isomers had the nitrile resonances separated by about 1.3 ppm; in the second they differed by less than 0.3 ppm in $CDCl_3$ and were unresolved in Me_2SO-d_6. It was surprising that the four values for the nitrile resonances in Me_2SO-d_6 (Table II) are almost identical (to within 0.2 ppm) with those of PBBC. A tentative assignment of cis and trans isomers was based on the greater volatility expected for the latter; additional confirmation was based on comparison with the vicinal and long-range coupling constants of chlorocyclobutane (**16**)[11] and *trans*-3-chlorocyclobutanecarbonitrile (**4**). At 250 MHz the ^{1}H NMR spectra of the two dimers gave essentially first-order splitting patterns for the H_1, H_6, and H_7 protons. The chemical shifts and coupling constants for these are compared with those for **4** and **16** in Table III.


14c

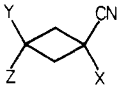

14t

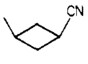
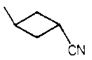
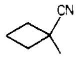
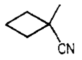

15c


15t

Proton NMR studies of a number of substituted cyclo-

Table IV
Changes in the Carbon-13 Chemical Shifts $\Delta\delta$ on Introducing Substituents X, Y, and Z into the Cyclobutanecarbonitrile Moiety[a]



X	Y	Z	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_3$	$\Delta\delta_{CN}$
Cl	H	H	28.47	12.06	-3.70	-2.76
H	Cl	H	-5.30	11.53	27.85	-1.91
H	H	Cl	-3.22	10.57	30.71	-0.97
H	OH	H	-9.17	9.61	43.28	0.55
H	H	OH	-6.63	10.79	44.91	0.75
	H	H	16.31 (16.71)	1.85 (1.88)	-3.54 (-3.64)	0.26 (0.13)
	H	H	16.77 (16.58)	2.63 (1.88)	-3.70 (-3.83)	0.30 (0.39)
H		H	-4.91 (-5.52)	1.98 (1.88)	18.07 (17.16)	-1.62 (-1.11)
H	H		-3.70 (-3.89)	1.23 (0.71)	18.56 (17.74)	0.04 (0.39)

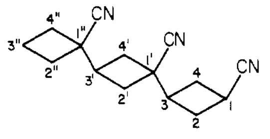
[a] In ppm; values in parentheses are those values obtained for the compounds measured in Me_2SO-d_6.

butanes have appeared.[6,11-15] Monosubstituted cyclobutanes[11] prefer one of the bent conformations, in contrast to the parent molecule in which the conformers are equally populated.[16] In chlorocyclobutane it has been shown[17] that the chlorine is primarily in the equatorial position. From the dihedral angles associated with the bent conformations, near equality can be expected between the vicinal coupling constants $^3J_{12}$ and $^3J_{14}$ and between the axial hydrogen on C1 and the axial and equatorial hydrogens on C2, respectively. If the ring were to approach planarity (or equilibrate between conformers in which the substituent is axial and equatorial), the first of these ($^3J_{12}$) should decrease and the second ($^3J_{14}$) should stay about the same. For example, these coupling constants are of comparable magnitude in chlorocyclobutane **16** and the dimer **14c**, whereas they differ by almost a factor of 2 in the trans compound **4** and the dimer **14t**.

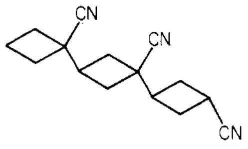
The long-range interproton coupling constants $^4J_{16}$ and $^4J_{17}$ provide additional support for the assignments of the stereochemistry of the two dimers; long-range H–H coupling constants between axial hydrogens ($^4J_{17}$ in Table III) are small and positive in sign, in contrast to those between axial and equatorial hydrogens ($^4J_{16}$), which are negative and have magnitudes of about 1 Hz. Thus, the conformity between the vicinal and long-range H–H coupling constants of **16** and **14c** as well as between **4** and **14t** are consistent with the assigned stereochemistry.

To remove the ambiguity in the assignment of the two nitrile resonances in the cis isomer, the 1-chloro derivatives **5**, **15c**, nd **15t** were synthesized (see Experimental Section). The chemical shifts were measured in chloroform-*d* and enetered in Tables I (**5**) and II (**15c** and **15t**). From these two tables it was possible to calculate the changes $\Delta\delta_C$ in the chemical shifts on introducing substituents X, Y, and Z into the cyclobutane-carbonitrile moiety. These substituent-induced changes are entered in Table IV. A most unusual result is the upfield shift (−2.76 ppm) of the CN due to the chlorine in the β- or C1-position. Clearly, this provides a method for assigning the nitriles of the two dimers. The chemical shifts of the chlorinated products were calculated by adding the $\Delta\delta_C$ values for X = Cl from Table IV to the chemical shifts of the dimers in Table II. In addition, it was assumed that the δ-substituent effect of a chlorine was 0.5 ppm and that the species present in greatest concentration (62%) was the cis isomer. Again, it is noted that the trans substituent has little effect on the nitrile resonance, whereas the cis substituent produces an upfield shift of about 1.5 ppm. The shifts of the ring carbons on Cl substitution are not as well reproduced, possibily due to 1,3-steric interactions, which are not present in **5** and **14t**.

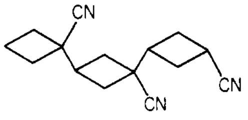
^{13}C NMR Spectra of the Four Trimers of Cyclobutanecarbonitrile. The four trimers **17cc**–**17tt**, which are based on the cyclobutanecarbonitrile moiety, were obtained in the course of preparing the dimers. As noted in the Experimental Section, the trimers were eluted from the column in the order **17tt**, **17ct**,**17tc**, and **17cc**, which is in conformity with the expected increase in the dipole moments. Moreover, the amounts of the trimers with cis ring fusions (**17ct** and **17tt**) were only about 15% of those with trans ring fusions (**17cc** and **17tc**). Because space-filling models for **17ct** and **17tt** suggest greater steric crowding than **17cc** and **17tc**, these might be expected to occur in lower yield.



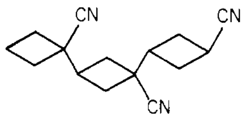
17cc



17tc



17ct



17tt

The ^{13}C chemical shifts of the four trimers, which were measured in $CDCl_3$ and Me_2SO-d_6, are entered in Tables V and VI, respectively. Also included are the calculated results, obtained on addition of the substituent shifts in Table IV to the chemical shifts of the dimers in Table II. The agreement between the experimental and calculated values, as evidenced by correlation coefficients near unity, provides strong evidence for the assignment of the four trimers. Some difficulties were encountered in the ^{13}C

Table V
Carbon-13 Chemical Shifts for the Four Trimers of Cyclobutanecarbonitrile Dissolved in $CDCl_3$ Compared with the Values Calculated from the Dimer Shifts[a]

	17cc		17tc		17ct		17tt	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
δ_1	17.26	17.25	18.40	18.46	17.39	17.25	18.60	18.46
δ_2, δ_4	29.38[b]	29.21	28.72[b]	28.46	29.72[b]	29.21	28.17[b]	28.46
δ_3	37.80	38.02	38.18[c]	38.51	38.27[d]	38.02	39.14	38.51
$\delta_{CN(C1)}$	120.47[c]	120.85	122.32[c]	122.51	120.66[e]	120.85	*f*	122.51
$\delta_{1'}$	33.20	33.56	33.83	34.02	35.40[d]	34.77	35.60	35.23
$\delta_{2'}$, $\delta_{4'}$	31.34	31.06	31.90	31.84	32.46[e]	30.31	32.83	31.09
$\delta_{3'}$	35.36	34.48	35.31	34.32	35.25	34.97	35.26	34.81
$\delta_{CN(C1')}$	120.96[c]	121.11	121.11	121.15	122.46[c,e]	122.77	*f*	123.11
$\delta_{1''}$	38.53	38.47	38.60	38.47	38.65[d]	38.93	39.17	38.93
$\delta_{2''}$, $\delta_{4''}$	28.97[b]	29.08	29.18[b]	29.08	30.00[b]	29.86	29.73[b]	29.86
$\delta_{3''}$	16.33	16.41	16.35	16.41	16.26	16.25	16.39	16.25
$\delta_{CN(C1'')}$	122.69	122.73	122.58[c]	122.70	122.75[c,e]	122.77	*f*	122.77
σ_s[g]	0.0019		0.0021		0.0045		0.0253	
σ_i[g]	0.1236		0.1386		0.3025		0.7983	
r[h]	1.0000		1.0000		0.9999		0.9977	

[a] Chemical shifts are measured downfield from internal Me_4Si; digital resolution at least 0.03 ppm. [b] The assignments of the methylene groups of the first and last rings are ambiguous: these assignments give a better overall fit of the calculated and experimental data. [c] The assignments of the nitrile carbons were ambiguous; this selection gives a better overall fit. [d] These assignments are tentative. [e] The signal-to-noise ratio was very low, but the signals were reproduced to within the digital resolution in two different runs. [f] Because of the small amount of material and very long relaxation time of the nitrile groups, the signal-to-noise ratio was not adequate to find these resonances; however, note that these were measured in Me_2SO-d_6 (Table VI). [g] Standard deviation in the slope and intercept, σ_s and σ_i, respectively. [h] Correlation coefficients.

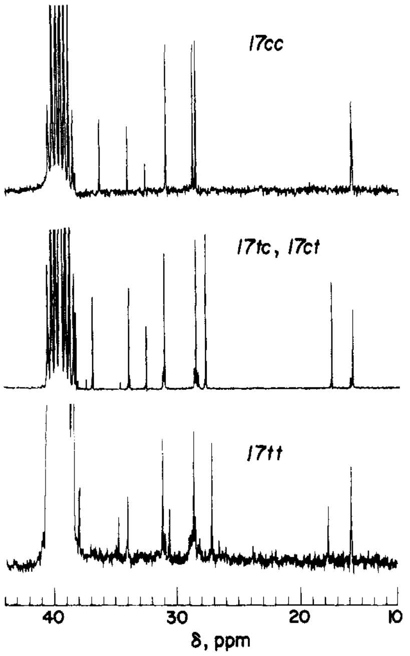


Figure 2. 62.90-MHz ^{13}C NMR spectrum of the ring carbons of **17cc**, **17tc**, **17ct**, and **17tt**. The strong solvent peak is due to Me_2SO-d_6. The nine distinct ring carbon resonances of **17cc**, **17tc**, and **17ct** can be seen clearly to high field of the solvent peaks; those for **17ct** are clearly resolved but have only 10–15% of the intensity of those for **17tc**. The ^{13}C spectrum of **17tt** (221 000 scans) exhibits several extraneous lines, which could be due to impurities in the solvent. Note that the resonances of the quaternary carbon C_1 for all trimers are only slightly upfield of the Me_2SO-d_6 multiplet.

assignments of **17ct** and **17tt** in $CDCl_3$ as noted in the footnotes to Table V. The 62.9-MHz ^{13}C NMR spectra of the ring and nitrile carbons, which were measured in Me_2SO-d_6, are depicted in Figures 2 and 3, respectively. Several lines in the spectra of **17tt** were assigned as impurities from relative intensities and pseudo-INEPT spectra. Although **17tc** and **17ct** were not separated, the assignment in Me_2SO-d_6 was easy because the resonances due to the latter were only 10–15% of the former (see Figures 2 and 3).

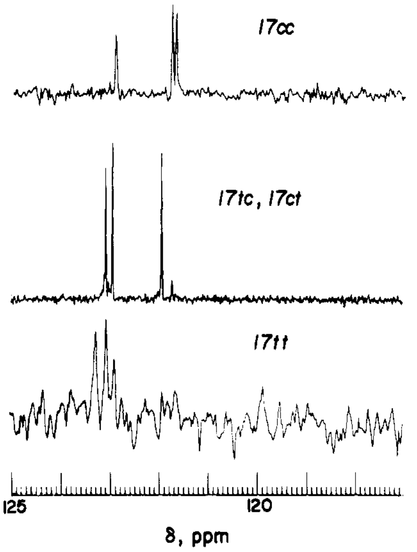


Figure 3. 62.90-MHz ^{13}C NMR spectra of the nitrile carbons of **17cc**, **17tc**, **17ct**, and **17tt** in Me_2SO-d_6. The three nitrile resonances assigned to **17ct** are only 10–15% of the intensity of those for **17tc**.

The spectra of the nitrile resonances of the four dimers in Figure 3 provide a clear indication of the cis effect; **17cc**, **17tc** and **17ct**, and **17tt** respectively have two, one, and no nitrile resonances at higher field. The monotonic increases in the standard deviations in proceeding from **17cc** to **17tt** in Tables V and VI arise primarily from the disparities in the chemical shifts of the central ring carbons. Possibly, this is due to the greater rigidity in this ring compared to the dimers from which the calculated results were obtained. It is most important to note that the nitrile resonances are exceedingly well reproduced in all cases.

The ^{13}C NMR data for the four trimers are of particular interest for the purposes of the study because it seems likely that the chemical shifts of the central cyclobutanecarbonitrile moiety should be close to those for

Table VI
Carbon-13 Shifts for the Four Trimers of Cyclobutanecarbonitrile Dissolved in Me_2SO-d_6 Compared with the Shifts Predicted from the Dimer Values[a]

	17cc		17tc		17ct		17tt	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
δ_1	15.77	16.05	17.53	17.68	16.01	16.05	17.70	17.68
δ_2, δ_4	28.50[b]	28.66	27.74[b]	27.49	28.36[b]	28.66	27.15[b]	27.49
δ_3	36.36	36.85	36.98	37.43	37.51	36.85	37.96	37.43
$\delta_{CN(C1)}$	121.71[c]	121.66	122.94[c]	123.16	121.72	121.66	122.93[c]	123.16
$\delta_{1'}$	32.64	32.76	32.60	32.63	34.73	34.39	34.76	34.26
$\delta_{2'}$, $\delta_{4'}$	30.96	30.54	31.10	30.54	31.25	29.37	31.16	29.37
$\delta_{3'}$	34.09	33.21	34.02	32.72	33.94	33.79	34.01	33.60
$\delta_{CN(C1')}$	121.79[c]	121.79	121.93	122.05	123.11[c]	123.29	123.32[c]	123.55
$\delta_{1''}$	38.36	38.28	38.34	38.15	38.18	38.15	38.03	38.15
$\delta_{2''}$, $\delta_{4''}$	28.75[b]	28.66	28.53[b]	28.66	28.68[b]	28.66	28.62[b]	28.66
$\delta_{3''}$	15.86	16.05	15.78	15.86	15.82	15.86	15.83	15.86
$\delta_{CN(C1'')}$	122.95	122.90	123.08[c]	123.16	123.02[c]	123.16	123.12[c]	123.16
σ_s[d]	0.0026		0.0033		0.0042		0.0079	
σ_i[d]	0.1723		0.2202		0.2807		0.5263	
r[e]	1.0000		0.9999		0.9999		1.0000	

[a] Chemical shifts in ppm downfield from internal Me_4Si; digital resolution at least 0.03 ppm. [b] The assignments of the two methylene resonances are ambiguous; in the case of **17tc** this choice gives a better overall fit. [c] The assignments of the nitriles are ambiguous; for **17cc** and **17tt** these choices give better overall fits. [d] Standard deviations in the slope and intercept, σ_s and σ_i, respectively. [e] Correlation coefficients.

PBBC (Figure 1). From Table VI it can be seen that the experimental values of the CN(C1′) resonances in Me_2SO-d_6 are 121.79 (or 121.71), 121.93, 123.11 (or 123.02), and 123.32 (or 123.12) ppm and are in reasonable conformity with the values of 121.70, 121.79, 122.95, and 123.04 ppm in PBBC. Quaternary carbons C1′ in the four trimers have resonances at 32.64, 32.60, 34.73, and 34.76 ppm, in reasonable accord with the several sharp lines near 32.7 and 35.2 ppm for PBBC in Figure 1. The methylene resonances for C2′ and C4′ are in a rather narrow range, 31.0–31.3 ppm, and almost certainly give rise to the broad resonance centered near 31.2 ppm in the PBBC spectrum. The methine carbons C3′ are in the range 33.94–34.09 ppm and would account for the broad resonance near 33.8 ppm in Figure 1. The rigidity of the PBBC backbone suggests long correlation times and short T_2's,[18,19] which would explain the observation that the CH and CH_2 resonances are quire broad in Figure 1. However, the resonances near 32.7 and 35.2 ppm are not predicted on the basis of the trimer results. Under the aggressive conditions of anionic polymerization with methyllithium, it is quite possible that impurities occur in the polymer.

Conclusions

The ^{13}C chemical shift of the nitrile group provides a method for differentiating between cis and trans isomers of 3-substituted (and 1,3-disubstituted) cyclobutanecarbonitriles; the nitrile resonance of the cis isomers is 1–1.5 ppm to high field of that for the trans isomer. Analogous effects for methyl resonances appear not to occur for the cis/trans-substituted methylcyclobutanes.

The appearance of four nitrile resonances in the ^{13}C NMR spectra of poly(bicyclobutane-1-carbonitrile) is consistent with chemical shifts obtained for the central cyclobutanecarbonitrile moiety of the four possible trimers **17cc**, **17tc**, **17ct**, and **17tt**. The substantially larger area of the highest field nitrile resonance implies that the largest fraction of PBBC has the rings trans fused as in **17cc**. A smaller proportion of the cyclobutanecarbonitrile moieties are trans fused as in **17tc** (121.8 ppm). The cis-fused rings such as in **17ct** and **17tt** lead to the resonances at 123.04 and 122.95 ppm in PBBC. These have a total area comparable to that for the cis–trans fusions. It would seem, intuitively, that cis fusions of the type in **17tt** would occur the least number of times in PBBC and perhaps the nitrile assignments for **17tt** should be reversed in Table VI (footnote *c*).

Experimental Section

Spectra. Both anionic- and free radical initiated PBBC were dissolved 0.3 g/mL in Me_2SO-d_6 (10-mm sample tubes), which served as solvent and internal lock. Chemical shifts were measured in ppm downfield from internal tetramethylsilane (Me_4Si). Carbon-13 spectra were observed at 22.63 MHz on a Bruker Instruments WH-90 FT NMR spectrometer (6024-Hz spectral widths collected into 4K data points), at 37.73 MHz on a Nicolet Magnetics NT-150 FT NMR spectrometer (5000-Hz spectral width collected into 32K data points, 12-mm sample tube), and at 62.90 MHz on a Bruker Instruments WM-250 FT NMR spectrometer (12000-Hz collected into 16K data points or 600 Hz collected into 4K data points). Spectra of the anionic-initiated PBBC were also obtained at 22.63 MHz with sulfolane, hexamethylphosphoramide, and $(CF_3)_2CHOH$ as solvents.

Carbon-13 NMR spectra of compounds **2**–**9** and **15** were obtained in 10-mm sample tubes at 22.63 MHz on the WH-90 spectrometer with chloroform-*d* as solvent and lock material (6024-Hz spectral widths collected into either 8K or 16K data points). Spectra of the dimers **14** and trimers **17** were also obtained at 62.90 MHz (12000-Hz spectral widths collected into 16K and 32K data points). In some cases the measurements were repeated in Me_2SO-d_6. In all cases chemical shifts were measured downfield from internal Me_4Si. The ^{13}C chemical shift assignments, which are thought to be firm unless noted otherwise, were based on single-frequency off-resonance decoupling, relative intensities, pseudo-INEPT,[20,21] and additivity relationships.[22]

The isomers of the chlorinated dimers **15** and **15t** were not separated; the assignments of the ^{13}C chemical shifts in Table II were based on the greater concentration (62%) of the cis isomer **15c**.

To remove ambiguities in the assignments of stereochemistry for the dimers **14c** and **14t**, ^1H NMR spectra of **3**, **4**, **12**, and **13** were obtained at 250.1 MHz on the WM-250 spectrometer. Samples were dissolved in $CDCl_3$ and the 5-mm samples tubes were degassed either by the freeze–thaw method or O_2 was displaced by bubbling dry N_2 gas through the samples. The ^1H NMR spectra of *trans*-3-chlorocyclobutanecarbonitrile (**4**) was analyzed by an iterative six-spin spectral simulation using Bruker Instrument's PANIC.81 computer program,[23] and the results are given in Table III. Unfortunately, the ^1H NMR spectra of the cis isomer **3**, which was complicted by the overlap of the α-CN resonance and the β-methylenes, was not analyzed.

Syntheses and Separation. All boiling points and melting points are uncorrected. Melting points were determined on a

Thomas-Hoover melting point apparatus. Infrared spectra were taken on a Perkin-Elmer 337 or 983 spectrophotometer between potassium bromide plates, between sodium chloride plates, or as a film. NMR spectra, which are reported in this section only, were obtained on a Varian Associates T-60 NMR spectrometer. Mass spectral data were collected on a Varian Mat 311A mass spectrometer. Preparative and analytical gas–liquid chromatography was done on a Varian Aerograph 1700 instrument. Elemental analyses were performed by Mic Anal. Inc., Tucson, AZ. Ultraviolet spectra were obtained on a Cary 14 spectrometer.

Poly(bicyclobutane-1-carbonitrile) (PBBC). Anionic PBBC was prepared by initiation with CH_3Li at −80 °C.[1,2] The inherent viscosity was 0.23 dL–g^{-1} at 0.5% in dimethyl sulfoxide. The polymer was also obtained under standard free radical conditions[1,2] (inherent viscosity 0.76 dL-g^{-1} at 0.1% in dimethylformamide).

Cyclobutanecarbonitrile (2) was obtained from Ash Stevens, Inc., Detroit Research Park, Detroit, MI, and the sample was redistilled before the NMR data were obtained.

***cis*- and *trans*-3-chlorocyclobutane-1-carbonitrile** (**3** and **4**) were obtained previously[1] as an 83:17 mixture of cis and trans isomers. The pure isomers were separated with a spinning-band column. The pressure was kept at 20 torr by water aspiration. One isomer was distilled at 120 °C oil bath, bp 99 °C (20 torr). The other isomer was distilled at 132 °C oil bath, bp 104 °C (20 torr). Each isomer was repeatedly distilled, and the reflux ratio was kept at 6:1.

The two isomers were identified first by gas chromatography. The chart rate was kept at 4 cm/min, bridge current at 150 mA, injection temperature at 300 °C, detector temperature at 185 °C, column temperature at 200 °C, and gas (helium) flow rate at 60 mL/min. The mixture of the two isomers showed two peaks at retention time 27 and 35 s, respectively. The 99 °C isomer showed a single peak at retention time 27 s and the 105 °C isomer at 35 s.

Chlorinations. All of the chlorination reactions were adapted from the literature procedure.[24]

1-Chlorocyclobutane-1-carbonitrile (5). A dry 25-mL three-neck, round-bottom flask was fitted with a reflux condenser, magnetic stir bar, and a nitrogen inlet. The apparatus was degassed by alternately evacuating and filling with nitrogen. With nitrogen flow through the system, phosphorus pentachloride (7.72 g, 0.037 mol) was added, and then the flask was sealed with rubber septums. To this was added via syringe with stirring 37.0 mL of dry chloroform, 3.90 g (0.0494 mol) of dry pyridine (caution: exothermic), and freshly distilled cyclobutane-1-carbonitrile (2.00 g, 0.0247 mol). This heterogeneous mixture was then brought to reflux and stirred for 47 h. At this time, the reaction mixture was cooled to room temperature and poured over 50 g of ice. After the mixture melted, the phases were separated and the aqueous portion was washed twice with ether. The combined organics were then washed twice with saturated potassium chloride solution followed by two 10% potassium carbonate washes. The organics were then dried over magnesium sulfate, filtered, and concentrated on a rotary evaporator. This was then bulb-to-bulb distilled at room temperature and 0.2 torr to yield 1.80 g (0.0156 mol, 63%) of 1-chlorocyclobutane-1-carbonitrile: ^1H NMR ($CDCl_3$), broad complex multiplet from δ 2.5 to 3.3 with a maximum at δ 2.8, broad complex multiplet from δ 1.9 to 2.5 with a maximum at δ 2.3 (these two envelopes overlap with that at lower field integrating for 60% of the total absorption); IR (neat), C–H, 2995, 2955, and 2880 cm^{-1} (s, s, m), C≡N, 2245 cm^{-1} (m); mass spectrum, *m/e* 117 (P + 2, 0.2%), 115 (P, 0.6%), 90 (17%), 88 (55%), 80 (base). Anal. Calcd for C_5H_6NCl: C, 51.97; H, 5.23; N, 12.12. Found: C, 52.18; H, 5.45; N, 12.02.

***cis*- and *trans*-3-Hydroxycyclobutane-1-carbonitrile (6 and 7).** These compounds were synthesized as described previously.[1] The 70:30 cis/trans mixture was not separated.

***cis*- and *trans*-1-Methyl-3-hydroxycyclobutane-1-carbonitrile (8 and 9).** The preparation was described previously;[25] no separation of isomers was attempted.

***cis*- and *trans*-3-(1-Cyanocyclobutyl)cyclobutane-1-carbonitrile (14c and 14t) and Trimers.** A 1-L, three-neck, round-bottom flask was equipped with a magnetic stir bar, an argon inlet, and a coarse sintered glass filter to which a second 1-L, three-neck, round-bottom flask was attached. All unused necks were securely sealed (all glassware and syringes had been baked dry in a 120 °C oven for 24 h). This apparatus was then alternately evacuated and filled with argon six to eight times.

Into this dry argon-filled reaction vessel was transferred 250 mL (0.0625 mol) of a freshly prepared 0.25 M (triphenylmethyl)sodium solution in ether via a 50-mL hypodermic syringe.[4] This was stirred in a 0 °C ice bath for approximately 10 min. To this chilled dark red solution was added a room-temperature solution of 4.9 g (0.06 mol) of dry cyanocyclobutane in 40 mL of anhydrous ether dropwise via a 50-mL hypodermic syringe. Time of addition was approximately 10 min. The pinkish precipitate of sodiocyanocyclobutane was then filtered with positive argon pressure and dissolved in 150 mL of freshly distilled tetrahydrofuran (from sodium/benzophenone). With a rapid flow of argon through the system, the apparatus was rearranged to accommodate a mechanical stirrer and dropping funnel (50 mL equipped with a side arm and a chilling bowl).

The reaction vessel was returned to the 0 °C bath, and a solution of 3.1 g (0.039 mol) of bicyclobutane-1-carbonitrile (prepared by the method of Hall et al.[1]) in 300 mL of dry tetrahydrofuran (from sodium/benzophenone) was prepared in a 500-mL round-bottom flask. This solution and the dropping funnel were each chilled with a dry ice/acetone cold bath. With vigorous stirring, the bicyclobutane-1-carbonitrile solution was added as a steady stream by cannulation from the 500-mL flask through the chilled dropping funnel into the reaction vessel. The time of addition was minimized (approximately 5 min), after which the reaction was quenched immediately with 8 mL of propionic acid.

The reaction mixture was then transferred to a 1-L round-bottom flask, concentrated on a rotary evaporator, and redissolved in ether. The salts and polymeric products were then filtered out, and the filtrate was concentrated again on a rotary evaporator. Most of the excess propionic acid and cyclobutanecarbonitrile were removed by vacuum distillation [25 °C (0.5 torr)]. The remaining crude organic product was dissolved in a minimum volume of acetone and applied to a silica gel column (22 cm × 2.5 cm, MCB Grade 12, 28–200 mesh) packed in hexane. This was eluted with hexane until all of the triphenylmethane remnants had been removed. The remainder of the organic product was eluted with acetone, reconcentrated, and subjected to Kugelrohr distillation. The volatiles were separated into four fractions. The distillate collected at a pressure of 0.3 torr and an oven temperature range of 80–90 °C was shown to be rich in the two dimers by gas chromatography. On the basis of peak areas the total yield of dimers in this distillate was 1.02 g (16% yield based on starting bicyclobutane-1-carbonitrile).

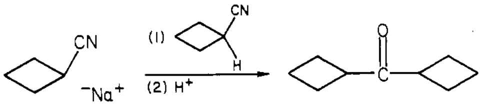
From the distillate 112 mg of one isomer and 165 mg of the other were isolated by preparative gas chromatography. The column used was 6 ft × $^1/_4$ in. Carbowax 6000 on Chromosorb (80–100 mesh). At a temperature of 200 °C and a helium pressure of 20 psi one isomer had a retention time of 180 s and the other a retention time of 310 s.

The trans isomer **14t** (retention time of 180 s) showed the following spectral characteristics: ^1H NMR ($CDCl_3$), two complex multiplets, one centered at δ 3.18 and the other centered at δ 2.4 (ratio of 1:2.5, respectively); IR (neat), C–H, 3000, 2960, and 2875 cm^{-1} (s, s, s), C≡N, 2250 cm^{-1} with a small shoulder at 2210 cm^{-1} (m, w); mass spectrum, *m/e* 160 (P, 0.76%); 159 (P − H, 5.6%); 133 (P − HCN, 9.2%); 107 (19.8%), 106 (P − 2HCN, 18.5%), 92 (24.7%), 79 (base), 52 (25.9%).

The isomer **14c** corresponding to a 310-s retention time shared the following spectral characteristics: ^1H NMR ($CDCl_3$), two broad overlapping multiplets, one centered at δ 3.0 and the other at δ 2.5 in a ratio of 1:10, respectively; IR (neat), C–H, 3000, 2960, and 2875 cm^{-1} (s, s, s), C≡N, 2250 and 2200 cm^{-1} (m, w); mass spectrum, *m/e* 160 (P, 1.8%), 159 (P− H, 18.8%), 133 (P − HCN, 18.5%), 107 (25.0%), 106 (P− 2HCN, 23.0%), 79 (base), 52 (P − $2C_5H_6N$ − HCN, 24.8%); high-resolution on *m/e* 160 and 159: $C_{10}H_{12}N_2$: calcd 160.1000, found 160.1059; $C_{10}H_{11}N_2$: calcd 159.0922, found 159.0946. Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.70; H, 7.70; N, 17.29.

Although our yields were not high, a variety of other attempts produced only trace amounts of the desired dimers (maximum ~0.6%). We believe that to produce the dimers of bicyclobutane-1-carbonitrile by this direct approach a compromise in conditions is necessary to minimize two competing side reactions.

Slow addition of a dilute, chilled solution of bicyclobutane-1-carbonitrile to a chilled reaction flask containing an excess of the anion derived from cyclobutanecarbonitrile minimizes the anionic polymerization of bicyclobutane-1-carbonitrile. Once dimers and trimers are formed, however, the nitrile groups are no longer involved in charge delocalization of carbanionic species in solution. In fact, the reaction of sodiocyclobutanecarbonitrile with 1 equiv of cyclobutanecarbonitrile at 0 °C produces upon protonation dicyclobutyl ketone as the only major product.



Our best results (16–21%) were achieved by adding the dilute (1%) chilled solution of bicyclobutane-1-carbonitrile as rapidly as possible through a chilled dropping funnel to the vigorously stirred carbanion solution.

1-Chloro-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (15c and 15t). The chlorination of cyclobutane-1-carbonitrile was performed again and monitored by NMR in order to estimate the time of reaction necessary for the chlorination of the dimers. By comparing the integrated intensities of the two envelopes observed in the proton NMR spectrum, it was judged the reaction was complete after 9 h. Each of the two dimers was then chlorinated by the same procedure described above with the exception that the reaction time was shortened to 9 h. Chlorination product from 3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (310-s retention time): 77 mg (0.48 mmol) of starting material yielded 53 mg (0.27 mmol, 52%) of chlorination product by Kugelrohr distillation [40–50 °C (0.1–0.05 torr)]; chlorination product from *trans*-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (180-s retention time): 36 mg (0.225 mmol) yielded 69 mg (0.35 mmol, 42%) of chlorination product by Kugelrohr distillation [(40–50 °C (0.1–0.05 torr)].

The spectral characteristics of these two chlorination products were identical: ^{1}H NMR (CDCl$_3$), broad complex multiplet at δ 1.9–2.4 with a maximum at δ 2.1, overlapping broad complex multiplet from δ 2.4 to 3.5 with a maximum at δ 2.85 (integration of the envelope at lower field corresponds to 54% of the entire absorption); IR (neat), C–H, 2990, 2945, and 2850 cm^{-1} (s, s, m); C≡N, 2240 cm^{-1} (s); mass spectrum *m/e* 196 (P + 2, 0.27%), 194 (P, 0.56%), 169 (7.35%), 167 (23.43%), 159 (82.27%), 79 (base). Anal. Calcd for $C_{10}H_{11}N_2Cl$: C, 61.70; H, 5.70; N, 14.39. Found from **14c**: C, 62.39; H, 5.85; N, 14.43; found from **14t**: C, 62.14; H, 5.77; N, 14.45.

Isomers of 3-[1-Cyano-3-(1-cyanocyclobutyl)cyclobutyl]-cyclobutane-1-carbonitrile (17cc, 17tc, 17ct, and 17tt). A ^{13}C NMR spectrum of the higher boiling fraction [92–110 °C (0.3 mmHg)] from the Kugelrohr distillation (vide supra) suggested the presence of higher molecular weight oligomers. This portion (~75 mg) was dissolved in a minimum volume of eluant and applied to a silica gel column (40 cm × 2.5 cm; column grade III/30 mm)[26,28] which was packed in eluant (a 1:7 mixture of acetone and hexane). One hundred and thirty 8-mL portions were collected and the solvent was evaporated. The first 25 fractions yielded a total of about 10 mg of impurities, one of which was identified by ^{13}C NMR as triphenylmethane. Fractions 60–75 yielded about 7 mg of a yellowish oil; the major component of this was identified as **17tt** from the ^{13}C NMR spectra (vide supra): ^{1}H NMR (CDCl$_3$), complex multiplets in the range 1.8–3; IR (CDCl$_3$), C–H, 2990 (shoulder), 2905 (shoulder), 2963, and 2859 cm^{-1}, C≡N, 2232, 2255 (shoulder) cm^{-1}.

The combination of fractions 76–91 gave about 25 mg of white crystalline needles, which were identified by ^{13}C NMR as a mixture of about 85% **17tc** and 15% **17ct**: mp 101.5–102 °C; ^{1}H NMR (CDCl$_3$), complex multiplets at δ 2.0–2.2, 2.4–2.6, 2.8, and 3.2; IR (CDCl$_3$), C–H, 2991, 2958, 2893, 2864 cm^{-1}; C≡N, 2254, 2232 cm^{-1}; mass spectrum, *m/e* 238 (P–H, 0.70%), 212 (P– HCN, 1.4%), 210 (3.7%), 194 (4.8%), 185 (P – 2HCN, 6.2%), 171 (3.8%), 159 (P – C_5H_6N, 4.6%), 157 (7.1%), 131 (5.5%), 106 (34.9%), 107 (44.8%), 92 (22.8%), 79 (base), 65 (12.0%), 61 (15.0%), 53 (28.9%), 52 (P – $2C_5H_6N$ – HCN, 44.0%). Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.28; H, 7.16; N 17.56. Found: C, 75.10; H, 7.11; N, 17.58.

Subsequent elutions of the column with a 1:1 mixture of acetone and hexane yielded on evaporation 10 and 14 mg, respectively, of white crystals in the first two 50-mL fractions. These were identified by ^{13}C NMR as **17cc**: mp 119–119.5 °C; ^{1}H NMR (CDCl$_3$), complex multiplets in the range δ 1–3; IR (CDCl$_3$), C–H, 2990, 2952, 2930 (shoulder), 2863 (shoulder); C≡N, 2254, 2232 cm^{-1}; mass spectrum, *m/e* 239 (P, 0.16%), 238 (P – H, 0.81%), 212 (P – HCN, 3.1%), 210 (4.3%), 185 (P – 2HCN, 6.3%), 171 (5.0%), 159 (P – C_5H_6N, 5.7%), 157 (8.3%), 131 (6.2%), 107 (39.7%), 106 (30.5%), 92 (21.4%), 79 (base), 65 (10.1%), 53 (24.2%), 52 (P – $2C_5H_6N$ – HCN, 34.2%).

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Analysis of the Pressure Dependence of the Crystallization Kinetics of *cis*-Polyisoprene

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ABSTRACT: Published crystallization kinetics data for *cis*-polyisoprene at pressures up to 3 kbar have been analyzed by using regime III of the Lauritzen–Hoffman theory and experimentally determined values of the input parameters T_∞, U^*, and $T_m°$. This theory was found to be applicable to such an analysis, and values of the fold surface free energy σ_e calculated confirmed the large and sudden increase in σ_e at a pressure approaching 1 kbar, found earlier independently from lamellar thickness data. A model has been proposed, involving a pressure-induced change in adjacent reentry fold conformation, to explain this behavior. The low values obtained for σ_e and the work of chain folding q have been tentatively attributed to low adjacent reentry fold fractions, suggesting that cilia emerging from the fold surface in regime III crystallization have low excess energies due to minimization of amorphous chain overcrowding.

1. Introduction

Pressure is a thermodynamic variable of obvious theoretical importance. It is also of considerable practical significance in polymer crystallization, since fabrication processes such as injection molding and extrusion apply high pressures to the polymer during crystallization. While complicating factors such as molecular orientation and nucleation density undoubtedly play very important roles in this process, an investigation of the effect of pressure on crystallization kinetics is an essential first step to understanding the crystallization of polymers during processing.

Some studies on polymer crystallization under pressure have been made, but most of them have been concerned with the morphology, particularly the "chain-extended" crystals produced in some polymers such as polyethylene. Kinetics studies seem to have been relatively ignored.

Phillips and Edwards[1] studied the crystallization kinetics of *cis*-polyisoprene (as the *Hevea* form of natural rubber) at pressures ranging from atmospheric to 3.5 kbar. This polymer was chosen because it could be stained with osmium tetraoxide for transmission electron microscopy, this staining technique serving also to stop the crystallization process at any given instant. Moreover, the relatively slow rate of crystallization at convenient temperatures and pressures simplified the experimental procedure. Growth rate and lamellar thickness data were obtained by transmission electron microscopy of thin films. The growth rate curves at any given pressure were bell-shaped, as expected. The application of pressure resulted in moving the curves to higher temperatures and in increasing the maximum growth rate over the first 1.5 kbar.

In this paper, we present an analysis of the high-pressure crystallization kinetics data of Phillips and Edwards[1] for *cis*-polyisoprene. The analysis of atmospheric-pressure data[2] has been reported earlier.[3] We have previously determined[4-6] the pressure dependence of the required input parameters U^*, T_∞, and $T_m°$.

2. Input Parameters

We have used the high-pressure crystallization kinetics data of Phillips and Edwards,[1] reported as linear growth rate G as a function of crystallization temperature T and pressure P, at pressures from atmospheric to 2.5 kbar. At each pressure, the WLF temperature T_∞ and WLF energy term U^* were calculated from the fitted[4] polynomials

$$T_\infty = -122.7 + 17.78P - 0.673P^2 \tag{1}$$

$$U^* = 17.26 + 1.57P - 0.099P^2 \tag{2}$$

and the equilibrium melting temperature $T_m°$ was calculated[6] from

$$T_m° = 35.5 + 27.0P - 1.49P^2 \tag{3}$$

where T_∞ and $T_m°$ are in °C, U^* is in kJ/mol, and P is in kbar. Equations 1 and 2 were fitted to dielectric data up to 3.8 kbar, and eq 3 was fitted to equilibrium melting data up to 2.6 kbar.

Values of the heat of fusion per unit crystal volume, Δh_f, are unavailable at high pressures and therefore had to be assumed invariant at the atmospheric-pressure value of 6.4×10^7 (J/m^3).[7] At least in the case of polyethylene this is a good approximation, as seen from the work of Karasz and Jones,[8] in which the heat of fusion per unit mass of crystal falls by no more than 2% over 1.6 kbar. Crystal dimensions, similarly, were assumed invariant at their atmospheric-pressure values: molecular width $a = 0.445$ nm and layer thickness $b = 0.623$ nm.[2] This is justified by the very low polymer crystal compressibilities normally encountered (typically ~1%/kbar).

The growth rate contours for *cis*-polyisoprene in the P–T plane are presented in Figure 1, together with the pressure dependence of the parameters T_∞ and $T_m°$. This figure clearly illustrates bounding of the crystallization temperature range by T_∞ and $T_m°$, as well as the movement of the entire range to higher temperatures with increasing pressure.

The temperature range $T_m° - T_\infty$ available for crystallization increases with pressure at a rate of about 14 °C/kbar, which is presumably the reason for the much higher maximum growth rates at high pressures. This observation contrasts well with that for *trans*-polyisoprene,[9] where the reduction in maximum growth rate with pressure was attributed to a narrowing of the range $T_m° - T_\infty$ at about 5 °C/kbar.

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