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Synthesis and Polymerization of Alkyl 1-Bicyclobutanecarboxylates

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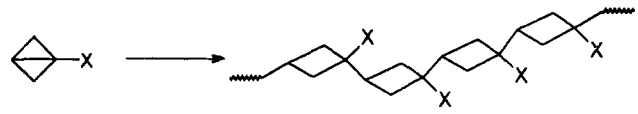
ABSTRACT: Bicyclobutane monomers substituted with an ester group at the 1 position were synthesized using a practical synthesis route, starting from 1,1-cyclobutanedicarboxylic acid, which is adaptable to the synthesis of various bicyclobutane esters and can be scaled up. Four new bicyclobutane monomers were prepared using this method, namely ethyl, isopropyl, β,β,β-trifluoroethyl, and phenyl 1-bicyclobutanecarboxylate. These bicyclobutanecarboxylates were subjected to free radical polymerization under various conditions. The bicyclobutane monomers behave very similarly to their vinyl counterparts. Chain transfer to polymer occurs to some extent, especially when the size of the substituent is relatively small (methyl ester). Excessively high molecular weights and gelation can be controlled by addition of a chain-transfer agent. The temperature, the size of the ester group, or the nature of the initiator has no marked influence on the stereochemistry of the bicyclobutane polymer backbones. Poly(methyl 1-bicyclobutanecarboxylate) is an optically clear material with a refractive index $n_D^{25} = 1.52$. Its resistance to thermal degradation is excellent. Polymers from this family exhibited surprisingly low T_g's, which probably result from an unexpectedly high flexibility of the bicyclobutane polymer backbone, as shown by molecular modeling.

Introduction

The opening of small strained carbon rings to form polymers has been of interest to polymer chemists for some time.[1] The relief of strain energy can provide a thermodynamic driving force for polymerization. Bicyclobutanes are one class of these highly strained monomers which have been under study in this laboratory.

The first synthesis of a bicyclobutane ring was reported by Wiberg[2] in 1959, who observed that ethyl bicyclobutane-1-carboxylate (**1b**) polymerized spontaneously when left at room temperature. Compounds containing a bicyclobutane ring remained a curiosity of organic chemistry, unknown to polymer chemists, for 10 years until Hall and co-workers[3-6] showed that bicyclobutanes carrying an electronegative substituent at the bridgehead position can polymerize and copolymerize through anionic or free radical ring-opening mechanisms, resulting in the incorporation of a cyclobutane ring in the polymer chain.

Incorporation of rings into polymers is often found to confer desirable thermal properties, including high glass transition temperature and high melting points. It is not coincidental that most polymers used commerically as films, fibers, and engineering plastics contain rings in the chain. The objective of the researchers of the Dupont Co., when they first investigated bicyclobutane monomers, was to find a substitute to acrylonitrile for the preparation of textiles fibers. Indeed, poly(1-cyanobicyclobutane) (**2**) was found to give a superior textile fiber,[7] with improved tensile properties and improved chemical and thermal stability. Only the high cost of the synthesis of the monomer prevented the commercial development.



1a, X = COOMe
1b, X = COOEt
1c, X = COOiPr
1d X = $COOCH_2CF_3$
1e, X = COOPh
2, X = CN

Although there are many reports concerning poly(1-cyanobicyclobutane), including synthesis and polymerization of the monomer,[3] thermal[8] and mechanical properties,[4] piezoelectric properties,[9] and NMR spectra,[10] very

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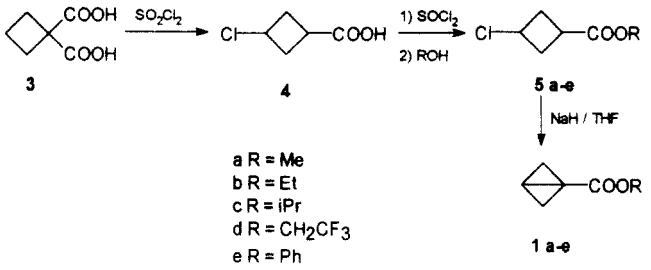
Scheme I



little work has been published on its ester analogues. Only the synthesis and polymerization of the methyl ester MBC **1a** and butyl ester have been reported,[4] as well as the NMR spectra and the stereochemistry of poly(methyl 1-bicyclobutanecarboxylate)[11] (PMBC). Recently, we reported the synthesis and polymerization of isopropyl 1-bicyclobutanecarboxylate[12] (**1c**) and the results presented here complete that work.

Our specific aims were to devise a practical synthesis route to bicyclobutane carboxylates, to study the thermal and optical properties of poly(bicyclobutanecarboxylates), and to evaluate them for applications as optical polymers. The novel polymers were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the refractive index of PMBC was also measured. The results will be discussed in the light of a molecular modeling study.

Results and Discussion

Synthesis of Monomers. The original synthesis of MBC (**1a**) by Hall,[4] starting from the cycloaddition of allene to acrylonitrile, is not without limitations. Overall, seven steps are necessary to prepare the monomer. Furthermore, the cycloaddition is a potentially hazardous reaction.

In a more direct and practical route, 1-bicyclobutanecarboxylates are prepared in this study in three flasks from readily available materials. The synthetic route, depicted in Scheme I, starts with the preparation of 3-chloro-1-cyclobutanecarboxylic acid (**4**) from 1,1-cyclobutanedicarboxylic acid (**3**), as described by Lampman et al.[13] The esterification of **4** was carried out using well-known methods. The esters **5** were converted to the respective bicyclobutanes **1a–e** using sodium hydride as a base to achieve dehydrochlorination, as previously described by Hall.[4] It was sometimes necessary to activate the reaction with a small amount of ethylene bromide or to use *N*-methylpyrrolidone as a cosolvent. The monomers were obtained as colorless oils and were purified by distillation. They were stored in a freezer at −50 °C in the presence of the free radical inhibitor 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide. This synthetic route is more direct and more practical than the previous method; 25% overall yield in three steps vs 20% overall yield in seven steps for the method of Hall.[4] It presents great versatility and can be easily scaled up to 100 g of monomer.

Polymerization. Solution, suspension, and emulsion polymerizations of methyl 1-bicyclobutanecarboxylate (**1a**) have already been reported.[4] However, very scarce information was given on the resulting polymers. Only inherent viscosities and the tendency to gel formation were reported.

The results of the polymerizations are presented in Tables I and II. The polymerization of 1-bicyclobutanecarboxylates **1a–e** could be initiated by thermal means, with or without initiator, by photochemical methods using AIBN, or via redox using $K_2S_2O_8$ and $FeCl_2$. The decomposition of the complex triethylborane/oxygen $BEt_3{\cdot}O_2$ at −50 °C[14] in tetrahydrofuran (THF) was also used to initiate **1a** polymerization.

The cyclobutane rings present in the polymer backbone can be either in a cis or in a trans configuration. In the case of **1a**, the cis/trans ratios were measured from the ^{13}C NMR signals of the methyl ester at 51 ppm, as described by Barfield[10] (Table I). The proportions of cis to trans ring enchainments in the polymers of the other bicyclobutane esters could be determined from the ratios of the intensities of the substituent and ring carbon ^{13}C resonances. Whatever the nature of the initiation and the polymerization conditions (temperature, solvent), about 66% of the rings were trans fused. Furthermore, about 66% of the rings were trans fused independent of the nature of the ester group. This result is more surprising in light of Barfield's[10] report that the pentad sequences in PMBC better conform to first-order Markov statistics than to Bernouilli triad statistics, as might be expected in a situation in which steric effects involving the substituents are substantial.

We anticipated that the size of the ester group would also influence chain transfer to the polymer chain and the molecular weight in the free radical polymerization process. Hall[4] ascribed the gelation tendency to chain transfer to polymer, resulting from the abstraction of the tertiary hydrogens of the bicyclobutane polymer by propagating radicals. In Figure 1, the GPC chromatograms of four PMBC polymers obtained with a free radical initiator in the presence of various amounts of a mild transfer agent (butyraldehyde) are shown. When small amounts of transfer agent were used, the corresponding molecular weight distributions were large and asymmetric. As the amount of added butyraldehyde increased, the shoulder corresponding to the higher molecular weights disappeared, the signal became more symmetric, and the yield of polymer decreased. This nicely illustrates the role of the transfer agent, which is to compete with the tertiary hydrogens on the polymer backbone in the reaction with the active end of the growing chains. Bulky ester groups prevent excessive branching and gelation. Nevertheless, GPC showed that the molecular weight distributions are still very broad, thus some branching is still taking place, but not enough to cause gelation.

Properties of Poly(bicyclobutanecarboxylate esters). Optical Properties. PMBC and the other poly(bicyclobutanecarboxylates) exhibited crystal clear transparency in the visible region. This good optical clarity can be attributed to the fact that bicyclobutane polymers obtained by radical polymerization exhibit very low or no crystallinity. This is an inherent property of many polymers containing ester groups in the side chain. In addition, the cis/trans stereochemistry of the cyclobutane rings in the polymer backbone must play an important role in preventing crystallinity. The good optical clarity can also be ascribed to the easy purification of the bicyclobutane monomers by distillation. Addition polymerization of these monomers gives very pure materials, as only catalytic amounts of initiator and additives are required.

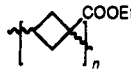
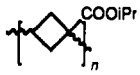
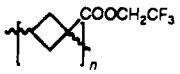
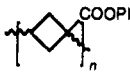
The refractive index of PMBC was measured at four different wavelengths. The results are reported in Table III. The refractive index of PMBC is higher than that of PMMA. Its dispersion is of the same magnitude, at least for the wavelengths considered. These materials could be used, for example, respectively as the core and as the cladding for the fabrication of a plastic optical fiber.

Table I
Free Radical Homopolymerization of Methyl 1-Bicyclobutanecarboxylate (MBC)

conditions[a]	initiation (3 mol %)	yield (%)	$[\eta]_{inh}$[b] (dL/g)	M_n	M_w	% cis linkages[c]
DMSO, 60 °C, [M] = 2 mol·L^{-1}, 16 h						
no transfer agent	AIBN	high	gel			
10 mol % Bual vs MBC	AIBN	68	0.76	32 200	68 700	34
5 mol % Bual vs MBC	AIBN	85	1.15	42 600	124 000	
2.50 mol % Bual vs MBC	AIBN	87	1.43	69 300	242 000	
1.25 mol % Bual vs MBC	AIBN	91	1.61			
0.65 mol % Bual vs MBC	AIBN	92	2.80	157 000	456 000	36
benzene, 5 °C, [M] = 2 mol·L^{-1}, 1 h	AIBN, $h\nu$	68	0.63	28 500	59 600	
toluene, 5 °C, [M] = 2 mol·L^{-1}, 1 h	AIBN, $h\nu$	59	0.59	17 700	40 200	34
THF, −50 °C, [M] = 2 mol·L^{-1}, 60 h						
5 mol % Bual vs MBC	BEt_3·O_2	high	gel			
25 mol % Bual vs MBC	BEt_3·O_2	72				29
std emulsion recipe						
16 h, 5 mol % Bual vs MBC	$K_2S_2O_8$	79	1.51	72 300		36
std suspension recipe						
16 h, 5 mol % Bual vs MBC	AIBN	75	1.17	43 000		35

[a] Bual: butyraldehyde. [b] Inherent viscosity in chloroform at 30 °C, concentration 0.5 g/dL. [c] From ^{13}C NMR.

Table II
Free Radical Homopolymerization of Bicyclobutanecarboxylate Esters

monomer	[M][a]	[AIBN][b]	T (°C)	solvent	[Bual][c]	yield (%)	$[\eta]_{inh}$[d] (dL/g)	$10^{-3}M_n$	$10^{-3}M_w$
	1.98	3	60	DMSO	0		gel		
	1.98	3	60	DMSO	5	78	2.68	581	835
	1.98	3	60	DMSO	25	75	0.55		
	1.32	0	60	DMSO	0	27	0.46		
	1.32	3	0, UV	CH_3CN	0	56	0.25	26	43
	1.32	0	0, UV	CH_3CN	0	0			
	1.7	3	60	DMSO	0	86	1.11	333	659
	1.7	3	60	DMSO	[tBu_3SnH] = 5	65	0.69	54	205
	1.38	3	60	DMSO	0	61	1.26		
	1.38	3	60	DMSO	5	95	1.19		
	1.85	0	60	DMSO	0	39	2.64		
	1.11	3	10, UV	DMSO	0	90	1.22		
	1.43	3	60	DMSO	0	78	1.23		
	1.43	3	60	DMSO	5	80	1.12		

[a] mol·L^{-1}. [b] mol % vs monomer. [c] Bual = butyraldehyde (mol % vs monomer). [d] Inherent viscosity in chloroform at 30 °C, concentration 0.5 g/dL.

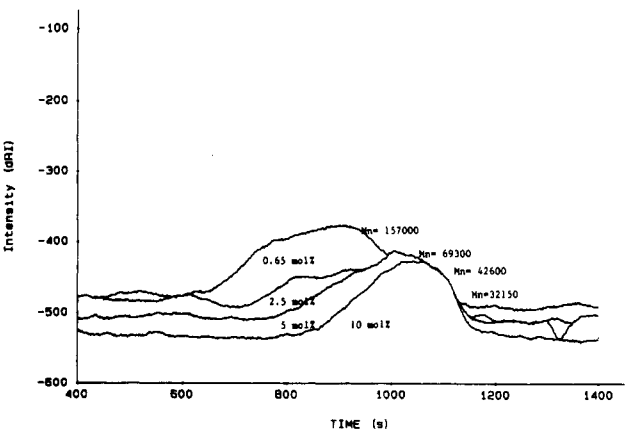


Figure 1. GPC curves of PMCB obtained by free radical polymerization in the presence of various amounts of butaraldehyde as chain-transfer agent.

Thermal Properties. The thermal decomposition of PMBC was analyzed by TGA, and the results are depicted in Figure 2a,b.[15] The decomposition in air starts slowly at 250 °C and accelerates around 370 °C. A second decomposition mode starts at 420 °C, as indicated by the derivative of the TGA signal. The decomposition is complete at 550 °C. The decomposition of PMBC under a flow of argon starts slowly at 300 °C and accelerates around 390 °C. A second decomposition mode starts at 420 °C. The decomposition is complete at 685 °C. We

Table III
Determination of the Refractive Index of a PMBC Film

wavelength (mm)	n	wavelength (mm)	n
0.4579	1.540	0.5145	1.524
0.4880	1.524	0.6328	1.521

can assume that the high strain associated with the bicyclobutane monomer prevents unzipping and depolymerization of PMBC. As a comparison, thermal degradation of PMMA under argon atmosphere occurs in the temperature range 230–390 °C to give back the monomer in quantitative yield.

The T_g's were measured by DSC under a flow of nitrogen at a heating rate of 40 °C/min.[16] The sample was cooled and the test repeated twice. Reproducibility between the second and third determinations was ±3 °C. A comparison between the poly(bicyclobutane esters) and the corresponding poly(methacrylate esters) is made in Table IV, showing that the two types of polymers exhibit similar T_g's. This result was highly unexpected. One would have assumed that the presence of a cyclobutane ring would considerably stiffen the backbone of the polymer, resulting in a higher T_g. This rigidity, for example, was invoked to explain the piezoelectric activity of poly(cyanobicyclobutane).[17]

We suggest that these surprisingly low T_g's result from an unexpectedly high flexibility of the bicyclobutane polymer backbone and will check this assumption by

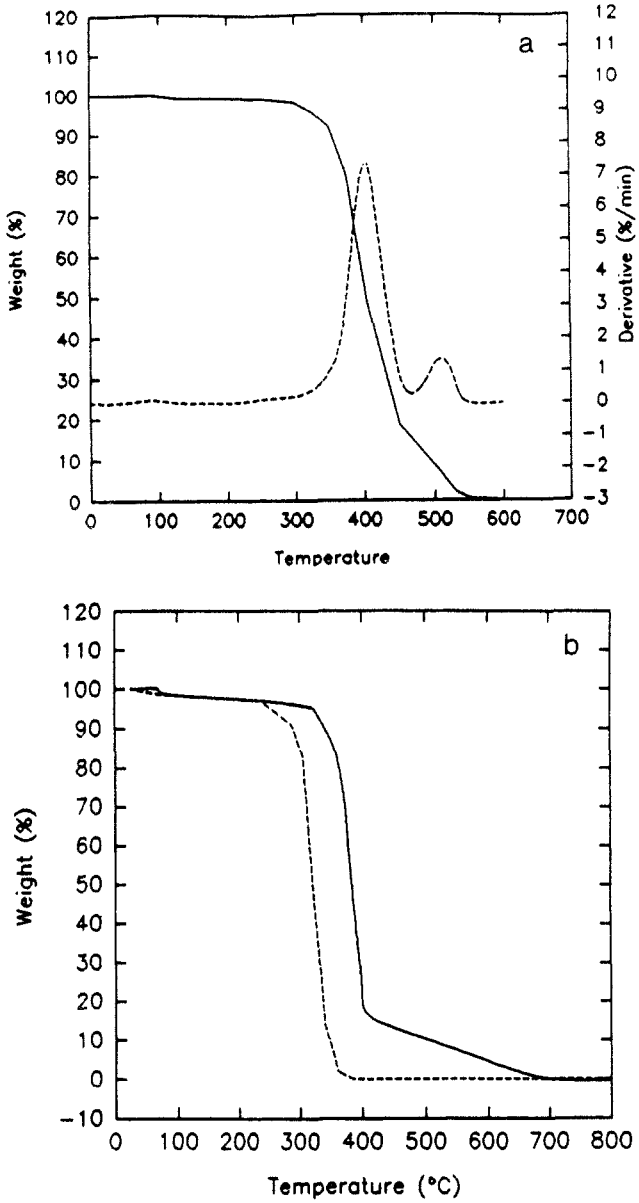


Figure 2. (a) TGA of PMBC (12.28 mg) heating at 5 °C/min under air flow. (b) TGA of PMBC (—) and PMMA (- - -) heating at 4 °C/min under argon flow.

Table IV
Glass Transition Temperatures (°C) of Bicyclobutanecarboxylates and Corresponding Methacrylate Polymers[a]

ester	bicyclobutanecarboxylate	methacrylate
methyl	95	105
ethyl	49	65
isopropyl	85	81
phenyl	120	110
CH_3CF_3	53	

[a] DSC, 40 °C/min, under N_2 flow.

molecular mechanisms calculations on poly(methyl 1-bicyclobutanecarboxylate) fragments.

Molecular Modeling and Flexibility of the PMBC Backbone. The backbone of PMBC is composed of alternating cyclobutane rings and σ bonds. If the backbone of this macromolecule is as flexible as a vinyl polymer backbone, it can only be the result of free rotation around the σ bonds. Accordingly, the rotational energy barrier around these bonds was investigated using molecular mechanics.

A fragment containing three cyclobutane rings was chosen as a model. The rotational angle θ was defined as

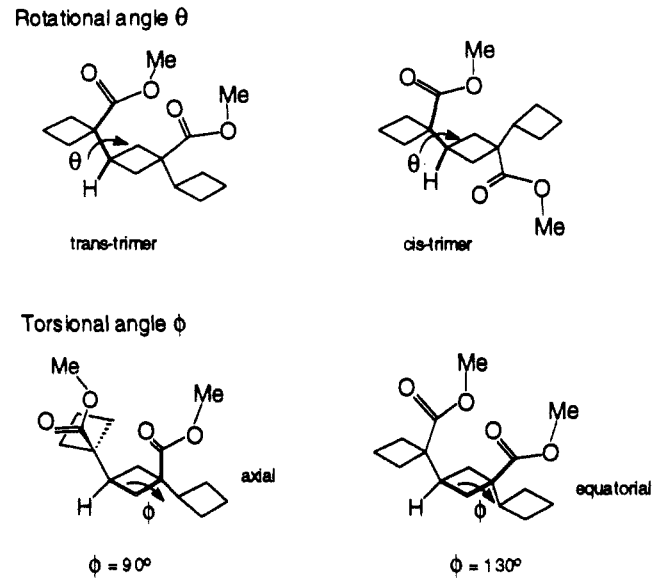


Figure 3. Rotational angle θ and torsional angle ϕ in PMBC trimer.

the angle between the tertiary hydrogen and the carbonyl carbon of the ester group when viewed along the σ bond (Figure 3). A cyclobutane ring can be either in a cis or in a trans configuration, and both cases were considered in the calculations.

Another important geometrical parameter is the puckering angle of the cyclobutane ring and the axial/equatorial conformations associated with the flipping of the ring (Figure 3). This puckering angle has been determined on small cyclobutane compounds by X-ray crystallography.[18] Depending on the size of the substituents, this angle varies between 180° (planar conformation) and 120°. There is generally a very small energy barrier between the axial and the equatorial substituents (between 0.5 and 1 kcal·mol^{-1} depending on the size of the substituents). The torsional angle ϕ was chosen to describe the conformation of the center cyclobutane ring. If the ester group is in an axial conformation, then $\phi = 90°$. If the ester group is in an equatorial conformation, then $\phi = 130°$.

Each trimer possesses a plane of symmetry. Thus the energy calculations need to be performed for θ only in the range 0–180°. The MM2 program[19] was used to calculate the rotational barrier energy as a function of θ (in 5-deg steps starting from the minimum at 180°). At each point, the structure was fully minimized, and the resulting torsional angle ϕ recorded. Electrostatic interactions were not included. The molecular modeling program SYBYL was used to view the resulting geometries.

The calculated rotational barrier diagram for the cis trimer is shown in Figure 4. There are three minima, at $\theta = 180°$, at $\theta = 60°$, and its symmetric counterpart at 300°. By analogy with the conformation of vinyl chains,[20] the optimum geometries were labeled as "anti" (T), "gauche" (G), and "gauche'" (G'), respectively. The energy barriers are very small: 4.5 kcal·mol^{-1} between the two gauche states (G → G') and 2 kcal·mol^{-1} between a gauche and the anti state (G → T). Careful examination of the optimum geometries revealed that there are no steric interactions between two successive ester groups, as is the case in a PMMA backbone. Instead, steric crowding occurs between the ester group and the hydrogens at the 2 and 2' positions of the central cyclobutane ring. The puckering or torsional angle of the central cyclobutane ring does not change much as the rotational angle θ varies. Both bulky cyclobutane ring substituents remain in equatorial con-

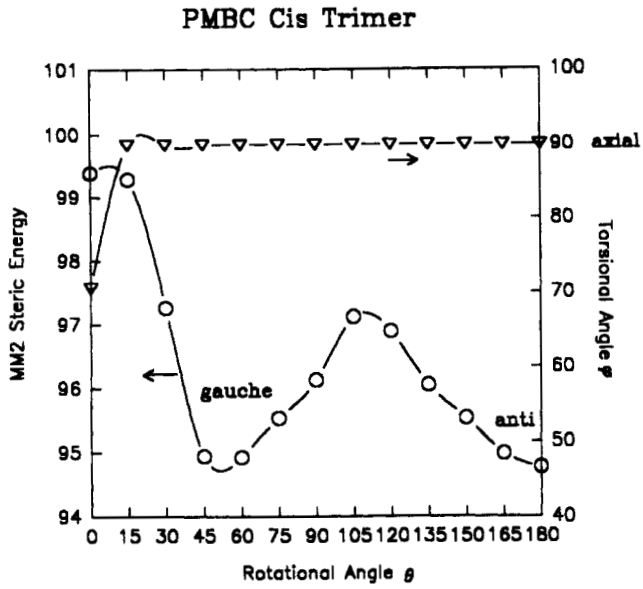


Figure 4. MM2 steric energy (O) and torsional angle ϕ (∇) as a function of the rotational angle θ for PMBC cis trimer.

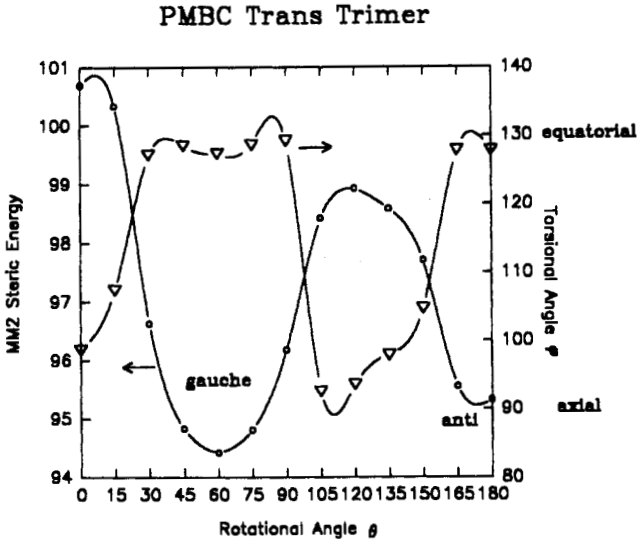


Figure 5. MM2 steric energy (O) and torsional angle ϕ (∇) as a function of the rotational angle θ for PMBC trans trimer.

formations and the ester remains axial, except when θ = 0°. At this point interactions between the ester group and the tertiary hydrogen force the latter more in an equatorial position.

The calculated rotational barrier diagram for the trans trimer is shown in Figure 5. Again, there are three minima, at θ = 180° (T), at θ = 60° (G), and its symmetric counterpart at 300° (G′). Surprisingly, the energy minima correspond to the G and G′ states. The T state is about 0.5 kcal·mol^{-1} higher in energy. This difference of energy is too small to have any significance at the MM2 level of calculation. However, these results shed light on the importance of the gauche states. The energy barriers are slightly higher than for the cis trimer, but still rather small: 6.5 kcal·mol^{-1} between the two gauche states (G → G′) and 4 kcal·mol^{-1} between a gauche and the anti state (G → T). As in the cis case, steric interactions take place between the ester group and the hydrogens of the central cyclobutane ring as rotation takes place around the backbone bond. For θ = 0° and θ = 120°, this cyclobutane ring is forced to invert and adopts a conformation with the ester group in the axial position. This results in a barrier of rotation G → T twice as high as in the preceding case.

Conclusion. An improved synthetic route to 1-bicyclobutanecarboxylate esters was developed, and the optical and thermal properties of the homopolymers are described for the first time. Molecular modeling suggests that the low glass transition temperature of PMBC and of the other poly(1-bicyclobutanecarboxylate esters) can be attributed to unhindered rotations around the σ bonds linking successive cyclobutane rings. The barriers of rotation were found to be the lowest in the case of the cis trimer. Based on these data, it is safe to assume that the ratio of cis/trans linkages will have a large influence on the flexibility of the backbone, and that all-trans bicyclobutane polymers should exhibit higher T_g's. In previous studies, it had been implicitly suggested that the most stable conformation for a bicyclobutane polymer would be the anti (T) state. Our results show that this is not always the case, and that the two gauche states cannot be neglected.

Experimental Section

Instrumentation. All reaction solvents were reagent grade and were distilled prior to use. GC–MS analyses were performed on a system consisting of a Hewlett-Packard Model 5890 gas chromatograph, a Model 5970 mass spectrometer, and an RTE-G/VM data system. ^{1}H and ^{13}C NMR spectra were obtained by using a Bruker WM 250 NMR or a Bruker AM 500 NMR spectrometer. Because of cis/trans mixtures and the complex spectra generally associated with cyclobutanes, spin–spin splitting was interpreted only in a few cases. Infrared (IR) spectra were recorded on a Perkin-Elmer 983 spectrometer. Microanalyses were performed by Desert Analytics, Tucson, AZ. A Dupont TGA 950 thermogravimetric analyzer was used under a flow of air or argon. Glass transition temperatures were measured on a Perkin-Elmer DSC-4 thermal analyzer under a flow of nitrogen.

3-Chloro-1-cyclobutanecarboxylic Acid (4). 1,1-Cyclobutanedicarboxylic acid (3) can be purchased from Aldrich or synthesized using a malonic ester synthesis. It is treated consecutively with thionyl chloride and sulfuryl chloride by following a literature procedure.[13]

Methyl 3-Chloro-1-cyclobutanecarboxylate (5a). The procedure described by Hall[4] was used: 151.9 g (1.13 mol) of 3-chloro-1-cyclobutanecarboxylic acid (4) was reacted with 30 mL of methanol and 175 mL of 2,2-dimethoxypropane in the presence of 1.10 g of methanesulfonic acid. NMR and GC analyses showed the product to be a 70/30 mixture of the trans and cis isomers. Yield: 133 g (78%).

Physical data: bp 96–105 °C (43 mmHg). The ^{1}H NMR and IR spectra were identical to the spectra reported by Hall et al.[4] ^{13}C NMR ($CDCl_3$), δ (ppm): 174.55 (C=O), 51.44 (C_3 cis), 50.72 (C_3 trans), 47.42 (CH_3 cis), 37.31 ($C_{2,4}$ cis), 36.70 ($C_{2,4}$ trans), 33.73 (C_1 cis), 32.13 (C_1 trans). Mass spectrum, *m/e*: 148 (2), 117 (22), 113 (95), 55 (102).

Ethyl 3-Chloro-1-cyclobutanecarboxylate (5b). 3-Chloro-1-cyclobutanecarboxylic acid (4) (23 g, 0.171 mol) was reacted with 32 mL of absolute ethanol in dry toluene (60 mL) with a catalytic amount of H_2SO_4 (five drops) using a Dean-Stark trap. After 3 h at reflux, no more water was collected and the mixture was cooled to room temperature and washed successively with water, with aqueous Na_2CO_3, and with water. The organic layer was dried over magnesium sulfate, and the volatiles were removed under reduced pressure. The residue was distilled under reduced pressure. NMR and IR analyses showed the product to be a 66/33 mixture of the trans and cis isomers. Yield: 22.17 g (80%).

Physical data: bp 85 °C (14 mmHg). IR (neat): 1736 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.59 (0.65 H, quint), 4.30 (0.35 H, quint), 4.15 (2 H, quad), 3.28 (0.65 H, sept), 2.81 (2.35 H, m), 2.55 (2 H, m), 1.26 (3 H, t). Mass spectrum, *m/e*: 134 (59), 127 (23), 117 (45), 99 (80), 89 (46), 55 (100), 53 (80). Anal. Calcd for $C_7H_{11}O_2Cl$: C, 51.69; H, 6.77. Found: C, 51.62; H, 6.82.

Isopropyl 3-Chloro-1-cyclobutanecarboxylate (5c). The acid chloride of 3-chloro-1-cyclobutanecarboxylic acid was prepared in quantitative yield using the procedure of Hall.[4] It was added (21.4 g, 0.139 mol) to a mixture of 2-propanol (12 g, 0.2 mol) and dimethylaniline (17.8 g, 0.146 mol). The mixture was

stirred at 60 °C for 3 h, then diluted in ether, and washed successively with a 0.1 M HCl solution, with water, and finally with a saturated solution of sodium carbonate. The organic layer was dried over magnesium sulfate and filtered, and the volatiles were removed under reduced pressure. Distillation afforded 17.8 g (yield 72.5%) of the product, whose ^{1}H NMR spectrum was identical to the spectrum described previously.[12]

β,β,β-Trifluoroethyl 3-Chloro-1-cyclobutanecarboxylate (5d). The acid chloride of 4 (20.5 g, 0.134 mol) was added drop by drop to 2,2,2-trifluoroethanol (16.75 g, 0.167 mol) cooled in an ice bath. The mixture was stirred at room temperature for 1 h, with slow and constant evolution of HCl, and then heated up to 100 °C to complete the reaction. When no more evolution of HCl could be detected, the mixture was cooled to room temperature and poured in 50 mL of water. The organic layer was washed successively with a saturated solution of sodium carbonate and with water, then dried over magnesium sulfate, and filtered. The volatiles were removed under reduced pressure, and the residue was distilled. NMR and GC analyses showed the product to be a 60/40 mixture of the trans and cis isomers. Yield: 21.1 g (73%).

Physical data: bp 91 °C (12 mmHg). IR (neat): 1748 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.59 (0.60 H, quint), 4.50 (2 H, m), 4.33 (0.40 H, quint), 3.41 (0.60 H, sept), 2.91 (0.40 H, m), 2.85 (2 H, m), 2.59 (2 H, m). ^{13}C NMR ($CDCl_3$), δ (ppm): 171.8 (cis) and 173.0 (trans) (C=O), 120.7 (trans) and 125.5 (cis) (CF_3), 61.44 (quadruplet × 2, CH_2 ester), 50.92 (cis) and 47.8 (trans) (CHCl), 37.0 (cis) and 37.31 (trans) ($C_{2,4}$ cis), 34.1 (trans) and 32.7 (cis) (C_1). Mass spectrum, *m/e*: 216 (7), 181 (62), 117 (24), 62 (100), 53(46). Anal. Calcd for $C_7H_8O_2F_3Cl$: C, 39.34; H, 3.74. Found: C, 39.62; H, 3.68.

Phenyl 3-Chloro-1-cyclobutanecarboxylate (5e). Phenol (13.58 g, 0.144 mol) was added to the acid chloride of 4 (20.1 g, 0.131 mol). The mixture was stirred overnight at 60 °C and then heated to reflux. The residue was directly distilled. NMR and GC analyses showed the product to be a 60/40 mixture of the trans and cis isomers. Yield: 26.3 g (95%).

Physical data: bp 101 °C (1.5 mmHg). IR (neat) 1768 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.35 (2 H, m), 7.21 (1 H, m), 7.05 (2 H, m), 4.62 (0.60 H, quint), 4.33 (0.40 H, quint), 3.50 (0.60 H, sept), 3.05 (0.40 H, m), 2.90 (2 H, m), 2.65 (2 H, m). ^{13}C NMR ($CDCl_3$), δ (ppm): 172.8 (trans) and 171.3 (cis) (C=O), 150.2, 129.1, 125.6 and 121.03 (C_{ar}), 50.63 (cis) and 47.42 (trans) (CHCl), 37.34 (trans) and 36.72 (cis) ($C_{2,4}$), 34.13 (cis) and 32.46 (trans) (C_1). Mass spectrum, *m/e*: 210 (17), 148 (2), 119 (30), 117 (104), 94 (26), 89 (54), 53 (70). Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.70; H, 5.22. Found: C, 62.91; H, 5.21.

General Procedure for Bicyclobutane Formation. A 200-mL three-necked flask was fitted with a condenser, an addition funnel, and a thermometer and was dried with a heat gun under vacuum. Sodium hydride (1.25 equiv), 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (0.05 g), and 40 mL of dry THF were introduced into the flask, and the mixture was stirred. A solution of the 3-chlorocyclobutane-1-carboxylate **5** (1 equiv) in 10 mL of dry THF was introduced into the addition funnel. As the addition began, the temperature of the mixture rose to 55 °C. After the addition, the mixture was heated at 60 °C for 2 h, until no more evolution of hydrogen was observed.

The mixture was cooled to −5 °C and washed with 10 mL of a saturated solution of potassium chloride. The aqueous phase was washed with 20 mL of THF. The organic layers were combined, dried with magnesium sulfate, and filtered. The solvent was removed under reduced pressure (0 °C, 10 mmHg). The pure bicyclobutane was distilled under vacuum while the receiver was chilled with dry ice. The yields are shown below.

Methyl 1-Bicyclobutanecarboxylate (1a). Yield: 78%. Physical data: bp 37 °C (10 mmHg). IR (neat): 1706 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$) (similar to the spectrum obtained by Hall[1] at 60 MHz), δ (ppm): 3.69 (3 H, s), 2.36 (2 H, m, exo), 2.09 (1 H, quintet, bridgehead), 1.15 (2 H, m, endo). ^{13}C NMR ($CDCl_3$), δ (ppm): 172.39 (C=), 51.00 (CH_3), 34.74 (C_1), 15.45 (C_3), 8.15 ($C_{2,4}$). Mass spectrum, *m/e*: 112 (19), 97 (8), 81 (28), 59 (18), 53 (100), 27 (65).

Ethyl 1-Bicyclobutanecarboxylate (1b). Yield: 65%. Physical data: bp 28–31 °C (1 mmHg). IR (neat): 1714 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.14 (2 H, quartet, J = 7.2 Hz, CH_2 ester), 2.33 (2 H, m, exo), 2.06 (1 H, quintet, bridgehead), 1.25 (3 H, t, J = 7.2 Hz, CH_3 ester), 1.12 (2 H, m, endo). ^{13}C NMR ($CDCl_3$), δ (ppm): 172.23 (C=O), 59.95 (CH_2), 34.98 (C_1), 15.55 (C_3), 13.76 (CH_3), 8.46 ($C_{2,4}$). Mass spectrum, *m/e*: 126 (10), 98 (61), 81 (26), 69 (24), 53 (100). Anal. Calcd for $C_7H_{10}O_2$: C, 66.66; H, 7.93. Found: C, 66.45; H, 7.97.

Isopropyl 1-Bicyclobutanecarboxylate (1c). Yield: 45%. Physical data: bp 28–30 °C (3 mmHg). IR (neat): 1716 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$) δ (ppm): 5.02 (1 H, sept), 2.34 (2 H, dd), 2.03 (1 H, m), 1.23 (6 H, d), 1.12 (2 H, dd). ^{13}C NMR ($CDCl_3$), δ (ppm): 172.34 (–C=O), 67.51 (CH), 35.19 ($C_{2,4}$), 21.60 (CH_3), 15.87 (C_1), 9.05 (C_3). Mass spectrum, *m/e*: 140 (13), 98 (175), 81 (87), 69 (50), 53 (165), 43 (262). Anal. Calcd for $C_8O_2H_{12}$: C, 68.57; H, 8.57. Found: C, 68.42; H, 8.55.

β,β,β-Trifluoroethyl 1-Bicyclobutanecarboxylate (1d). Yield: 75%. Physical data: bp 40–41 °C (9 mmHg). IR (neat): 1739 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.49 (2 H, quartet, J = 9.2 Hz, CH_2 ester), 2.41 (2 H, m, exo), 2.23 (1 H, quintet, bridgehead), 1.24 (2 H, m, endo). ^{13}C NMR ($CDCl_3$), δ (ppm): 171.19 (C=O), 120.81 (CF_3), 60.0 (CH_2 ester, quartet, J = 37 Hz), 35.62 (C_1), 17.77 (C_3), 8.13 ($C_{2,4}$). Anal. Calcd for $C_7H_7F_3O_2$: C, 46.46; H, 3.88. Found: C, 46.43; H, 3.98.

Phenyl 1-Bicyclobutanecarboxylate (1e). Yield: 81%. Physical data: bp 50–51 °C (2 mmHg). IR (neat): 1761 cm^{-1} (ester). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.2 (5 H, m, phenyl), 2.52 (2 H, m, exo), 2.34 (1 H, quintet, bridgehead), 1.30 (2 H, m, endo). Mass spectrum, *m/e*: 174 (4), 145 (4), 116 (7), 94 (10), 81 (38), 53 (100). Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.86; H, 5.74. Found: C, 75.89; H, 5.82.

Polymerizations. The solvents and reagents were carefully dried by common procedures. The monomers, stored at −50 °C in the presence of inhibitor, were freshly distilled prior to use. Isobutyraldehyde or tri-*n*-butyltin hydride were used as transfer agents. In some cases, no initiator or transfer agent was necessary to obtain polymer. The reaction products were isolated and purified by three consecutive precipitations from chloroform in a large excess of cold methanol. The white powders were ground and dried in a drying pistol (3 mmHg, in the presence of phosphorus pentoxide, heated with water). The resulting polymers were soluble in common organic solvents such as DMF, DMSO, acetone, chloroform, benzene, and toluene. They were insoluble in methanol and water. Nice films could be cast from toluene solutions and analyzed by IR. The reported molecular weights were obtained by GPC in chloroform using Phenomenex 10^5, 10^4, and 10^3 Phenogel columns and are relative to polystyrene standards. Inherent viscosities were measured in chloroform, using 50 mg of polymer in 10 mL at 30 °C.

Solution Polymerization. In a polymerization tube were successively introduced 1.5 mL of a DMSO solution of butyraldehyde and 0.5 mL of methyl 1-bicyclobutanecarboxylate (2 mol·L^{-1}). AIBN (0.015 g) was added, and the solution was degassed by three freeze–thaw cycles. The system was sealed under vacuum and heated overnight at 60 °C.

Photochemical Initiation Polymerization. In a polymerization tube were successively introduced 1.5 mL of benzene or toluene and 0.5 mL of methyl 1-bicyclobutanecarboxylate (2 mol·L^{-1}). AIBN (0.015 g) was added, and nitrogen was bubbled through the solution for 30 min. The system was sealed cooled at 5 °C and irradiated for 1 h with a UV lamp.

Suspension Polymerization. A 100-mL aqueous solution of butyraldehyde (1.42 g) and of poly(vinyl alcohol) (0.3 g) was prepared. This solution (1.75 mL) was introduced into a polymerization tube, and 0.5 mL of monomer (1.77 mol·L^{-1}) and 0.015g of AIBN were added. Nitrogen was bubbled through the solution for 30 min. The system was sealed under nitrogen. The reaction mixture was virgorously stirred and heated at 50 °C overnight.

Emulsion Polymerization. The two following solutions were prepared: (A) a 100-mL aqueous solution containing 1.42 g of Tween 20 [poly(oxyethylene sorbitan monolaurate)], 1.42 g of butyaldehyde, and 1 g of $FeCl_2$; (B) a 165-mL aqueous solution containing 0.5 g of $K_2S_2O_8$ and 1 g of borax. In a polymerization tube were introduced successively 1.75 mL of solution A, 0.5 mL of solution B, and 0.5 mL of monomer. Nitrogen was bubbled through the solution for 30 min. The system was sealed under nitrogen. The reaction mixture was vigorously stirred and heated

at 50 °C overnight. The resulting polymer was isolated by freeze-drying and purified by reprecipitation in methanol.

Solution Polymerization at −50 °C. In a polymerization tube were successively introduced via syringe 10 mL of THF, 0.25 mL of butyraldehyde, and 1 mL of methyl 1-bicyclobutanecarboxylate (0.85 mol·L^{-1}). The solution was degassed by three freeze–thaw cycles and cooled at −50 °C. A solution of BEt_3 in hexane (0.25 mL, 1 mol·L^{-1}) was introduced via syringe under nitrogen, followed by 3 mL of oxygen. The tube was sealed and kept over the weekend in a freezer at −50 °C.

Poly(methyl 1-bicyclobutanecarboxylate). ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$), δ (ppm): 3.70 and 3.66 (3 H, cis and trans CH_3 ester), 2.74, 2.56 and 2.48 (1 H, CH), 2.28 (2 H, CH_2 exo), 2.0 (2 H, CH_2 endo). ^{13}C NMR ($CDCl_3$), δ (ppm): 176.88 and 176.27 (carbonyl cis and trans), 52.3 and 51.76 (CH_3 cis and trans), 46.25 and 44.02 (C cyclobutane), 35.16 and (33.53 and 33.09) (CH cyclobutane, cis and trans), 29.37 and 28.84 (CH_2 cyclobutane). IR (film cast from benzene): 1727 cm^{-1} (ester). DSC (heating rate 40 °C/min): T_g = 95 °C. Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.28; H, 7.17. Found: C, 64.44; H, 7.22.

Poly(ethyl 1-bicyclobutanecarboxylate). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.12 (2 H, CH_2 ester), 2.6 (1 H, CH), 2.27 (2 H, CH_2 exo), 2.02 (2 H, CH_2 endo), 1.28 (3 H, CH_3 ester). ^{13}C NMR ($CDCl_3$), δ (ppm): 176.68 and 176.10 (carbonyl cis and trans), 60.71 and 60.50 (CH_2 ester), 46.49 and 44.16 (C cyclobutane), 35.29, 33.61 and 33.24 (CH cyclobutane), 29.26 and 28.78 (CH_2 cyclobutane), 14.29 (CH_3 ester). IR (film cast from acetone): 1712 cm^{-1} (ester). DSC (heating rate 40 °C/min): T_g = 45 °C. Anal. Calcd for $(C_7H_{10}O_2)_n$: C, 66.66; H, 7.93. Found: C, 66.02; H, 7.92.

Poly(β,β,β-trifluoroethyl 1-bicyclobutanecarboxylate). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.48 (2 H, CH_2 ester), 2.7 (1 H, CH), 2.38 (2 H, CH_2 exo), 2.17 (2 H, CH_2 endo). ^{13}C NMR ($CDCl_3$), δ (ppm): 174.59 and 173.89 (carbonyl cis and trans), 122.98 (CF_3, quartet, J = 277 Hz), 60.40 (CH_2 ester, quartet, J = 36 Hz), 46.44 and 44.05 (C cyclobutane), 34.58 and 33.37 (CH cyclobutane), 28.67 (CH_2 cyclobutane). IR (film cast from acetone): 1746 cm^{-1} (ester). DSC (heating rate 40 °C/min): T_g = 45 °C. Anal. Calcd for $(C_7H_7F_3O_2)_n$: C, 46.66; H, 3.88. Found: C, 46.68; H, 3.84.

Poly(phenyl 1-bicyclobutanecarboxylate). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.25 (3 H, aromatic H), 6.98 (2 H, aromatic H), 2.97 (1 H, CH), 2.67 (2 H, CH_2 exo), 2.32 (2 H, CH_2 endo). ^{13}C NMR ($CDCl_3$), δ (ppm): 174.42 (carbonyl), 150.82 and 150.65 (aromatic C_1, cis and trans), 129.43, 125.84 and 121.43 (aromatic C), 48.88, 47.11 and 44.58 (C cyclobutane), 35.32 and 33.72 (CH cyclobutane), 29.16 (CH_2 cyclobutane). IR (film cast from acetone): 1765 cm^{-1} (ester). DSC (heating rate 40 °C/min): T_g = 120 °C. Anal. Calcd for $(C_{11}H_{10}O_2)_n$: C, 75.86; H, 5.74. Found: C, 75.95; H, 5.79.

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