Macromolecules 1983, 16, 1544–1546

Notes

Structural Analysis by ^{13}C NMR of Copolyethers of 2-Methyloxacyclobutane and 2-Methyloxacyclopentane

JØRGEN KOPS* and HANS SPANGGAARD

Instituttet for Kemiindustri, Technical University of Denmark, DK-2800 Lyngby, Denmark.

Received October 6, 1982

Introduction

Substitution of the five-membered oxacyclopentane ring (THF) is known to have an adverse effect on the polymerizability by ring opening. Thus methyl substitution at the 3-position results in the formation of only relatively low molecular weight polymers.[1] Recently, the kinetics and thermodynamics of polymerization of 3-methyloxacyclobutane have been investigated.[2] Methyl substitution at the 2-position has been found to effectively prevent polymerization,[3] although oligomerization also has been reported.[4] However, it has been found that 2-methyloxacyclopentane may form copolymers with other cyclic ethers.[5-7] Such copolymerization studies have recently been carried out also with 3,4-dimethyloxacyclopentane.[8] We have studied the polymerization of the four-membered 2-methyloxacyclobutane and obtained information about the ring opening by structural analysis of the polymers by ^{13}C NMR.[9,10] In continuation of these studies we have investigated the copolymerization with 2-methyloxacyclopentane and we report here our findings concerning the ring opening of this monomer based on the structural analysis of the copolymers.

Experimental Section

Materials. The monomer, 2-methyloxacyclobutane (2-MOCB), was prepared as previously described.[9] Commercial 2-methyloxacyclopentane (2-MOCP) was distilled on a spinning-band distillation apparatus and found by GC to be more than 99.99% pure. The monomers were dried over BaO and Na–K alloy.[11] The initiator Et_3OPF_6 and CH_2Cl_2 were purified according to a previously published procedure.[11] The model ether, the diethyl ether of 1,4-pentanediol, was prepared by reacting 5.8 mmol of 2-MOCP with 5.2 mmol of Et_3OPF_6 in 6.7 mL of CH_2Cl_2 at 0 °C for 5 days before addition of 11 mmol of dry ethanol. The workup consisted of neutralization with NaOH, drying with $CaCl_2$, and evaporation of low-boiling components at 50 °C and 20 mbar. The ^{13}C NMR spectrum showed only nine sharp carbon signals (ppm relative tetramethylsilane): 15.3, 15.6, 19.8, 26.0, 33.3, 63.7, 66.1, 70.8, and 74.9.

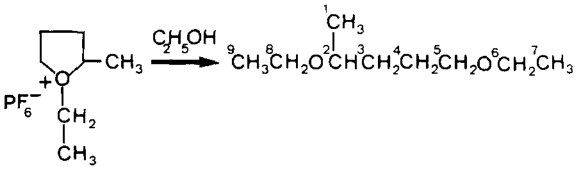
Polymerization. All polymerizations were carried out by using standard high-vacuum techniques. The polymerizations were stopped by addition of 1–2 mL of ethanol or THF with 5% water; however, the 2-MOCB polymerization at −30 °C was stopped by addition of 2.5 mL of 0.067 M NaOPh solution (in THF).

Characterization. Molecular weights were determined by gel permeation chromatography using THF solvent.[10] A Waters Model 200 instrument equipped with polystyrene gel columns (porosities 10^3, 10^4, 2×10^4, and 10^6 Å) was used. On the basis of a calibration curve obtained with narrow molecular weight polystyrenes, approximate weight-average molecular weight values were calculated by applying the extended chain length method, using a Q value (weight per Å) of 15.4. The ^{13}C NMR spectra were obtained in deuteriochloroform at room temperature with tetramethylsilane as internal reference on a Bruker WH90 FT spectrometer operating at 22.63 MHz.

Results and Discussion

The polymerization results are summarized in Table I. For comparison, data from the homopolymerization experiments with the two monomers are included. The yields of the copolymers are intermediate between the yields of the homopolymers. 2-MOCP gives very low yields of oligomers under the same conditions where the more strained 2-MOCB yields high polymers in high yields. The molecular weights of the copolymers are also lowered due to the presence of the five-membered ring monomer 2-MOCP. The actual content of this monomer in copolymers prepared from a 50:50 mixture is found to be around 10% from spectroscopic analysis (see below).

The attempted homopolymerization of 2-MOCP yielded in one experiment, when ethanol–water was used to terminate the reaction, mainly the diethyl ether of 1,4-pentanediol as determined by ^{13}C NMR analysis:



The following signals were observed in the ^{13}C NMR spectrum (ppm relative to tetramethylsilane): CH_3, 19.8; C-2, 75.0; C-3, 33.3; C-4, 26.0; C-5, 70.8; C-6, 66.1; C-7, 15.3; C-8, 63.6; C-9, 15.6. These values are in accordance with the values observed for the model ether. In addition, the values were also in good agreement with those calculated from the previously investigated model ether for poly(2-MOCB), the diethyl ether of 1,3-butanediol,[9] and the appropriate values for the influence of neighboring C and O atoms in α, β, γ, and δ positions on the chemical shift for the carbon in question.[12,13] By increasing tenfold the amount of initiator added relative to the monomer, somewhat higher yields of oligomers were obtained; however, we conclude, in accordance with previous investigators, that high polymers are not obtainable from 2-MOCP.

Our reported investigation of the structure of poly(2-MOCB)[9] has revealed considerable tendency for formation of head-to-head (HH) and tail-to-tail (TT) units when the polymers are prepared with cationic initiators, while a regular head-to-tail (HT) structure is obtained with a coordination initiator.[10]

A ^{13}C NMR spectrum for a copolymer is shown in Figure 1. One may readily recognize the signals from the 2-MOCB units, including HH and TT units in accordance with those reported for the homopolymer.[9] In Table II are listed the assignments of the signals attributed both to the 2-MOCB units, which correspond closely to the previously reported values,[9] and to the 2-MOCP units, for which the signal assignments will be discussed below. In Table III are tabulated the differences in the number of interactions between the carbons in the two types of units in the copolymer in the various triads listed in Table IV and the predicted influence on the chemical shift values. We may disregard any interactions from atoms in ϵ positions or further removed from the carbons in question since the influence on the chemical shift has been shown to be small.[12,13] It is easily shown that for the carbons of each of the repeat units the number of interactions is the same irrespective of whether the adjoining units arise from the same or other monomers. The actual numbers of interactions for any given carbon in the two types of units are, however, different, and these numbers vary for the various

0024-9297/83/2216-1544$01.50/0

Table I
Copolymerization of 2-MOCB and 2-MOCP

2-MOCP,[a] mol L^{-1}	2-MOCB,[a] mol L^{-1}	Et_3OPF_6,[a] mol L^{-1} × 10^2	temp, °C	time, h	polymer yield, wt %	$\overline{M}_n \times 10^{-3}$ [b]	$\overline{M}_w \times 10^{-3}$ [b]	2-MOCP[c] in copolymer, mol %
1.8	1.8	3.6	0	475	32			9
1.8	1.8	3.6	−30	715	54	6.6	12.3	10
7.9	0	6.7	0	261	1.2			
3.3	0	3.3	−30	714	1.5			
0	2.7	2.9	0	2	95	2.5	6.6	
0	1.7	0.27	−30	2.5	90	22	84	

[a] Polymerization carried out in methylene chloride solution. [b] Determined by gel permeation chromatography in THF. [c] Estimated from the intensities of the ^{13}C NMR signals arising from the 2-MOCP units relative to the total intensities of the corresponding carbon signals from both 2-MOCB and 2-MOCP units of the copolymers.

Table II
^{13}C NMR Signals in Copolymers of 2-MOCP and 2-MOCB[a]

2-MOCP

CH_3			C-2							C-5	
HT	HH		HT	HH		C-3		C-4		HT	TT
a	b	c	d	e	f	g	h	i	j	k	l
19.8	20.5	21.3	75.2	72.9	72.1 (?)	33.4	34.1	26.1	26.4	68.7	71.1

2-MOCB

CH_3			C-2							C-4	
HT	HH		HT	HH		C-3				HT	TT
a′	b′	c′	d′	e′	f′	g′	g″	h′	h″	k′	l′
19.8	20.5	21.3	72.6	70.6	69.7	37.0	37.4	37.6	38.0	65.1	67.6

[a] Chemical shifts (ppm) relative to tetramethylsilane and signal labeling in accordance with Figure 1.

Table III
Predicted ^{13}C NMR Chemical Shifts for 2-MOCP in Copolymers with 2-MOCB

triad	interacting atom	difference in interactions (β, γ, and δ effects) for carbons in 2-MOCP relative to similar atoms in 2-MOCB and corresponding calculated shift values, ppm									
		CH_3		C-2		C-3		C-4[a]		C-5[b]	
A	C O	$+\delta$ $-\delta$	0.0	$+\gamma - \delta$ $-\gamma + \delta$	3.5	$+\beta - \gamma - \delta$ $-\beta + \delta$	−4.5	0 $-\beta + \delta$	−16.0	0 $-\gamma + \delta$	6.1
B	C O	$+\delta$ $-\delta$	0.0	$+\gamma - \delta$ $-\gamma + \delta$	3.5	$+\beta - \gamma + \delta$ $-\beta + \gamma$	−4.5	$-\delta$ $-\beta + \gamma$	−16.3	 $-\gamma + \delta$	6.1
C	C O	$+\delta$ $-\delta$	0.0	$+\gamma - \delta$ $-\gamma + \delta$	3.5	$+\beta - \gamma$ $-\beta + \gamma$	−4.2	$-\delta$ $-\beta + \gamma$	−16.3	 $-\gamma + \delta$	6.1
D	C O	$+\delta$ $-\delta$	0.0	$+\gamma - \delta$ $-\gamma + \delta$	3.5	$+\beta - \gamma$ $-\beta + \gamma$	−4.2	0 $-\beta + \gamma$	−16.0	0 $-\gamma + \delta$	6.1

[a] Relative to C-3 in 2-MOCB. [b] Relative to C-4 in 2-MOCB.

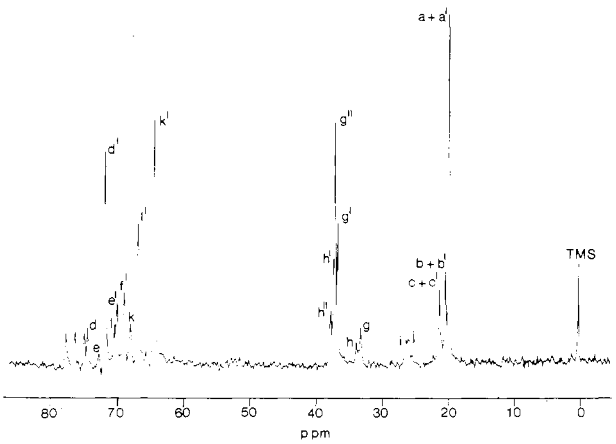
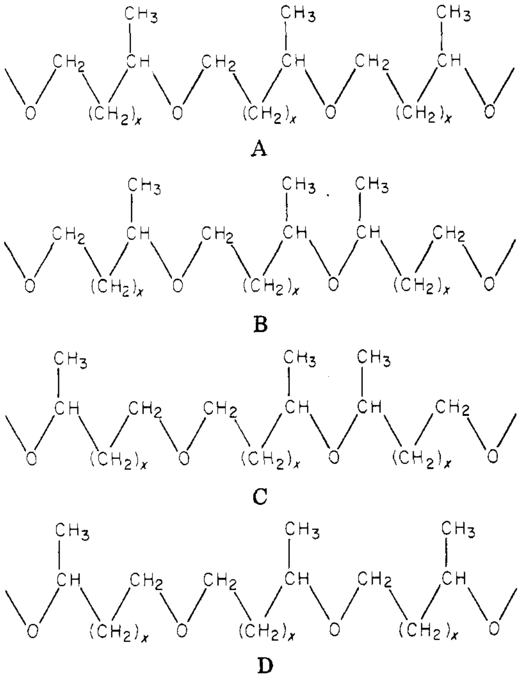


Figure 1. ^{13}C NMR spectrum of the copolymer of 2-MOCB and 2-MOCP prepared at −30 °C.

triads. The β, γ, and δ parameter values for the interactions are a little different for C and O,[12,13] and in Table III are listed separately those arising from the two different atoms. Consider as an example how the difference in interactions between the two repeat units is found in the case of C-2 with neighboring C and O atoms in triad A. With reference to Table IV one counts the following number of α, β, γ, and δ interactions: 2-MOCP, 2, 2, 2, 1; 2-MOCB, 2, 2, 1, 2; the difference amounts to $+\gamma - \delta$. With respect to O atoms the α, β, γ, and δ interactions are as follows: 2-MOCP, 1, 0, 0, 1; 2-MOCB, 1, 0, 1, 0; the difference corresponds to $-\gamma + \delta$. On this basis the following shift value is calculated from published parameters: $-2.3 - 0.3 - (-5.8) + 0.3 = 3.5$ ppm. For the carbons in 2-MOCP chemical shifts are predicted relative to those in 2-MOCB as follows: CH_3, no shift; C-2 and C-5, downfield shifts; C-3 and C-4, upfield shifts. In addition, for the latter carbons slightly different signals are predicted from units in different triads. These predictions may be compared with the actually observed signals in Table II. However, in this connection the meso–racemic isomerism for the HH units, which causes additional splittings, must also be considered. In accordance with the prediction, the presence of the 2-MOCP units does not give rise to additional CH_3 signals. The methine carbon signals (C-2) are displaced about 2.5 ppm downfield, roughly according to prediction, and the configuration of the signals is un-

Table IV
Triad Structures in Copolymers of 2-MOCB and 2-MOCP[a]



[a] $x = 1$ for 2-MOCB units; $x = 2$ for 2-MOCP units.

altered, corresponding to a major signal from the HT units and two signals from the HH units, one of which (signal f) appears to coincide with the large signal from the C-2 in 2-MOCB in the HT configuration around 72.6 ppm. The methylene carbons in 2-MOCP adjacent to oxygen (C-5) give signals that are displaced downfield according to prediction, although to a smaller extent. The fact that two signals are observed with nearly the same separation as for 2-MOCB indicates the formation of TT units. Finally, the other two methylene carbons in 2-MOCP give signals that show upfield shifts, in accordance with prediction, when compared with 2-MOCB.

The values for 2-MOCP in Table II are also in good agreement with the signal positions already given for the diethyl ether of 1,4 pentanediol. In this connection it should be noted that the signal for C-5 in the diethyl ether is in close agreement with the TT signal listed in Table II, in agreement with the structural similarity.

The amounts of 2-MOCP in the copolymers were estimated on the basis of the intensities of the signals from the various carbons relative to those of the reference carbons in the 2-MOCB plus the 2-MOCP units. The values calculated on this basis were 9 and 10% for the copolymers prepared at 0 and −30 °C, respectively. Since both copolymers were prepared from equal molar feed ratios, the reactivity of 2-MOCP is obviously much lower than that of 2-MOCB. The copolymer prepared at lower conversion at 0 °C contained a relatively smaller amount of the less reactive monomer.

Stereoisomerism is not observed for the copolymers under the conditions employed. However, we have previously shown that tacticity may be detected in poly(2-MOCB), particularly when the NMR analysis is performed with a more powerful instrument.[9,10] For the 2-MOCP units, the chiral carbons are in ϵ positions in the HT units and the tacticity effects are expected to be very small, if observable at all.

Registry No. Et_3OPF_6, 17950-40-2; 2-MOCP-2-MOCB copolymer, 86101-64-6.

References and Notes

(1) Chiang, R.; Rhodes, J. H. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 643.
(2) Garrido, L.; Guzmân, J.; Riande, E. *Macromolecules* **1981**, *14*, 1132.
(3) Rose, J. B. Ref 6 in "The Chemistry of Cationic Polymerization"; Plesch, P. H., Ed.; Pergamon Press: Oxford, 1963; p 433.
(4) Pruckmayer, G.; Wu, T. K. *Macromolecules* **1973**, *6*, 33.
(5) Tsuda, T.; Nomura, T.; Yamashita, Y. *Makromol. Chem.* **1965**, *86*, 301.
(6) Yamashita, Y.; Tsuda, T.; Okada, M.; Iwatsuki, S. *J. Polym. Sci., Part A-1* **1966**, *4*, 2121.
(7) Tsuda, T.; Yamashita, Y. *Makromol. Chem.* **1966**, *99*, 297.
(8) Malanga, M.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2033.
(9) Kops, J.; Hvilsted, S.; Spanggaard, H. *Macromolecules* **1980**, *13*, 1058.
(10) Kops, J.; Spanggaard, H. *Macromolecules* **1982**, *15*, 1200.
(11) Hvilsted, S.; Kops, J. *Macromolecules* **1979**, *12*, 894.
(12) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
(13) Lindeman, L. P.; Adams, J. C. *Anal. Chem.* **1971**, *43*, 1245.

On the Radial Structure of Kevlar

S. B. WARNER*

Celanese Research Company, Summit, New Jersey 07901.
Received December 13, 1982

A great deal of activity has appeared in the literature relating to various aspects of the structure of du Pont's commercial lyotropic polymer fiber Kevlar, poly(*p*-phenyleneterephthalamide) (see, for example, ref 1–9). One unique feature of Kevlar, which has been pointed out by Blades,[1] is that Kevlar, unlike most other synthetic fibers, is *not* transversely isotropic. This circularly symmetric birefringence in the crosss section, or lateral birefringence, is extremely difficult to measure;[1] however, it is an important structural feature that seems to be absent from a number of the proposed structural models. In this paper an alternative, simpler technique for assessing lateral birefringence is outlined.

One technique that can be used to examine radial/circumferential structure is interference microscopy, albeit the technique is generally restricted to assessment of skin–core birefringence or thicknesses. Interference microscopy, originally outlined by Faust[10] and used over the years by several microscopists,[11-13] has shown a recent revival[14,15] primarily because it is the basis of a patent claim to Frankfort and Knox[16] on high-speed spinning of poly(ethylene terephthalate) (PET). In this case, the high skin–low core birefringence seems to develop because of the materials' response to temperature gradients along the diameter of the fiber during spinning. The technique, however, can also be employed to assess lateral birefringence under appropriate conditions.

The procedure for obtaining the necessary interference micrographs of fibers consists of immersing a filament in a liquid of refractive index n_L such that the maximum fringe displacement, d_{max}, is about half the fringe spacing, D. Polarizer or analyzer must be oriented appropriately. Three interference micrographs are required (four independent ones are possible) for analysis of $n_{F_\parallel}$ and $n_{F_\perp}$, the indices of refraction of the fiber parallel and normal to the fiber axis, respectively, and t, and the thickness of the fiber, as a function of radial position. The conditions employed in this study are as follows: $n_{L_1} = 1.592 < n_{F_\perp}$ (A in Figures

---

* Present address: Kimberly-Clark Corp., Neenah, WI 54956.

0024-9297/83/2216-1546$01.50/0