

Thermal Decomposition of Poly(oxytetramethylene) Glycol

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ABSTRACT: Studies of thermal decomposition on poly(oxytetramethylene) glycol have been conducted by pyrolysis gas chromatography–mass spectrometry, infrared spectroscopy, and thermogravimetric analysis (TGA). The major volatile decomposition products are suggested to be a series of molecules made up by the repetition of oxytetramethylene with formyl and/or methyl ends. Absorption peaks, associated with formyl appear in infrared spectrum of a sample preheated at 523°K lower than the onset temperature obtained from the TGA curve. The isothermal TGA curves fit well to the Shihma rate equation for the random decomposition of polymers. The proper activation energies obtained from the thermally controlled and the isothermal TGA data are approximately 60–70 kJ mol⁻¹ and lower than those for other polymers in ordinary thermal decomposition. These data suggest that the major reaction in the thermal decomposition of poly(oxytetramethylene) glycol is an ether cleavage. Two pathways, a radical scission accompanied by β -hydrogen transfer and a nonradical reaction through a four-membered ring transition state, are proposed and discussed for the ether cleavage. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1538–1544, 2000

Key words: decomposition mechanism; poly(oxytetramethylene) glycol; thermogravimetric analysis; pyrolysis gas chromatography–mass spectrometry

INTRODUCTION

Poly(oxytetramethylene) (POTM) obtained by ring-opening cationic polymerization^{1,2} of tetrahydrofuran is important to the industries of rubber, foam, etc., for having excellent energy-storing capacity. POTM is end-linked by use of diisocyanate for industrial applications. We previously studied the swelling behaviors for end-linked POTM dimethacrylate copolymers.^{3,4} In the pyrolysis gas chromatography/mass spectrometry (PGC/MS) conducted for determination of the copolymer composition, the evolution of a large amount of aldehydes and of a small amount of tetrahydrofuran was observed. This is a very interesting comparison with the evolution of a large amount of ethylene oxide in the thermal decom-

position of poly(oxyethylene).⁵ The excellent energy-storing capacity is attributed to its low melting temperature responsible for the thermal instability. The thermal decomposition studies are helpful in success of the molding.

In this connection, the present research efforts focus on the thermal decomposition behavior of a linear POTM glycol (POTMG). From the thermal decomposition products identified by PGC/MS, two pathways (Scheme 1) are proposed for the evolution of aldehydes. They are discussed on the basis of the infrared (IR) spectra of the decomposition residues and the thermogravimetric analysis (TGA) data.

EXPERIMENTAL

Materials

POTMG (TERATAN 2900, DP = 40), kindly provided by E. I. duPont de Nemours & Co., was used

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Table I Relative Intensities of Major Fragment Peaks for Thermal Decomposition Products from Dibutyl Ether

<i>m/Z</i>	Relative Intensity					
	Prod. 1 Ether	Butane	Prod. 2	Butanal	Prod. 3	Dibutyl
27	32	37	68	59	14	13
28	34	33	20	15	6	11
29	43	44	75	54	28	25
39	10	13	28	23	8	8
41	39	28	65	60	24	33
42	19	12	26	12	s	s
43	100	100	85	79	s	s
44	s	s	100	100	s	s
56	s	s	s	s	10	7
57	s	s	32	26	100	100
58	22	18	s	s	s	s
71	n	n	11	7	n	n
72	n	n	60	73	n	n
87	n	n	n	n	14	14
130	n	n	n	n	n	n
r.t./min	4	u	13	13	27	27

Prod., product; s, slight; n, noise; u, unknown; r.t., retention time.
The data on butane are cited from Reference 12.

without further purification for the PGC/MS, IR, and TGA experiments.

PGC/MS Techniques

A tandem connection of a Shimadzu PYR 2A pyrolyzer, a Varian 1440 gas chromatograph, and an Anelva NEVA TE-600 mass spectrometer was

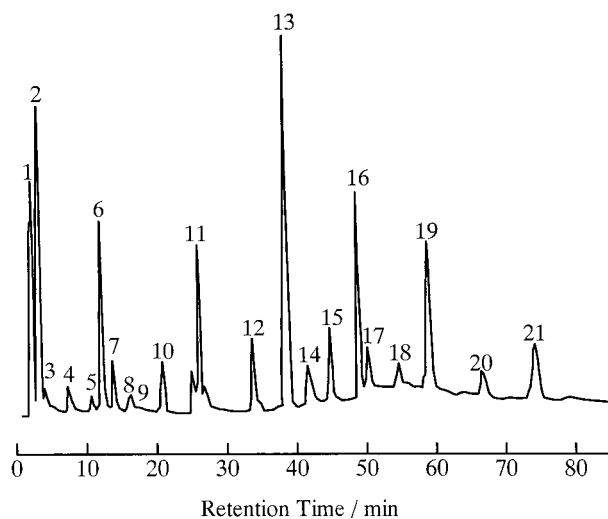


Figure 1 A pyrogram of POTMG thermally decomposed at 773°K.

used. Measurements were performed under conditions previously described elsewhere⁶: pyrolyzer temperature, 773°K; GC column size, 3-mm diameter, 4-m length; GC column temperature, from 303 to 523°K (4°K min⁻¹); MS total emission current, 213 μ A; MS electron energy, 70 V; MS ion energy, 12 V; potential of MS secondary electron multiplier, 2.00 kV; flow rate of helium (carrier gas), 51 cm³ min⁻¹; sample size, approximately 5 mg (precisely weighed). Thermal decomposition products were identified by comparing their retention times and mass spectra with those of the reference compounds. The PGC/MS data on the reference compounds were obtained under the same conditions. Agreement between the mass spectral peaks of a sample and a reference was judged by referring to the mass numbers of their apparent parent peaks and the mean of distances between the respective relative intensities for the seven largest fragment peaks.⁷

IR Spectroscopy

All IR spectra were obtained for samples in potassium bromide discs by use of a JASCO FT/IR-230 IR spectrophotometer. Samples were heated at 423, 443, 463, 473, 483, and 523°K for 10 min in a nitrogen gas flow. The optical densities were obtained by drawing appropriate straight lines

Table II Relative Intensities of Major Fragment Peaks for Products 2, 6, 7, and 11 from POTMG and Reference Compounds

<i>m/Z</i>	Relative Intensity							
	Prod. 2	Butane	Prod. 6	Butanal	Prod. 7	THF	Prod. 11	Dibutyl Ether
27	31	37	77	59	27	25	14	13
28	30	33	33	15	22	20	9	11
29	39	44	88	54	20	25	28	25
39	17	13	42	23	24	25	11	8
40	s	s	s	s	14	16	n	n
41	40	28	81	60	60	69	33	33
42	16	12	23	12	100	100	s	s
43	100	100	87	79	27	26	s	s
44	s	s	100	100	8	s	s	s
56	s	s	s	s	n	n	10	7
57	s	s	29	26	n	n	100	100
58	s	18	s	s	n	n	s	s
71	n	n	9	7	39	44	n	n
72	n	n	58	73	39	40	n	n
87	n	n	n	n	n	n	15	14
r.t./min	4	u	13	13	17	17	27	27

Prod., product; s, slight; n, noise; u, unknown; r.t., retention time.
The data on butane are cited from Reference 12.

and thereby subtracting the background intensities.

TGA Techniques

A Perkin-Elmer 7 Series thermogravimetric analyzer was used. Sample sizes were approximately 1.2 mg (precisely weighed). The TGA curves are not reproducible, perhaps because of the thermal instability of solid-state of POTMG.^{8,9} To make the thermal history uniform, the samples were isothermally preheated at 353, 363, and 373°K for 10 min in the thermogravimeter, followed by measurement of the mass losses at constant heating rates. TGA curves at 20°K min⁻¹ were obtained for the samples with 2.5 wt % of hydroquinone, preheated at 373°K. Nitrogen gas was used to flow around the sample pan during measurement. The isothermal TGA techniques were also conducted for determination of the type of thermal decomposition.

The activation energies were obtained from the TGA curves at heating rates of 2, 5, 10, and 20°K min⁻¹, by the isoconversion method,¹⁰ using the Doyle approximation¹¹ of p-function, and from the isothermal TGA curves observed at 483 and 498°K by fitting them to the first-order and the random decomposition curves.

RESULTS AND DISCUSSION

Decomposition Products

Table I shows the results of PGC/MS on dibutyl ether. The products 1, 2, and 3 are identified as butane, butanal, and dibutyl ether, respectively. No peak due to either butanol or 1-butene appears within the detection limit. These suggest that formyl and methyl ends are formed by a cleavage of the ether bonds and that hydrogen abstraction of a butoxyl free-radical formed by a radical scission of the ether bonds is a minor reaction.

Figure 1 shows a representative pyrogram of POTMG. Products 2, 6, 7, and 11 are identified as butane, butanal, tetrahydrofuran, and dibutyl ether, respectively, by referring to the retention times and mass spectra of the reference compounds obtained by PGC/MS run under the same conditions, as shown in Table II. The mass spectra of the other major products have a relatively large peak at *m/Z* = 44, perhaps due to the H₂C=CH—OH radical cation¹³ formed by β-bond cleavage with transfer of a single hydrogen atom in aldehydes, not considered to be due to the other radical cations, as shown in Table III. Table III also shows that these mass spectra have no peaks

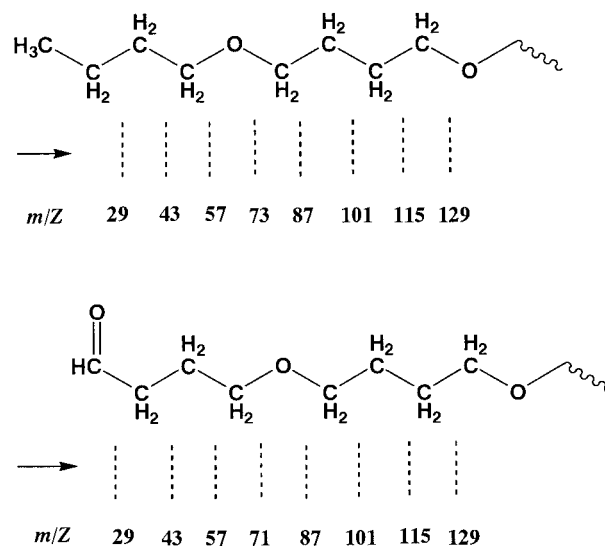
Table III Relative Intensities of Major Fragment Peaks for Major Thermal Decomposition Products from POTMG

<i>m/Z</i>	Relative Intensity										
	Product										
10	12	13	14	15	16	17	18	19	20	21	
17	8	9	7	16	16	14	13	17	10	10	15
18	29	35	27	100	100	52	90	100	42	78	77
26	s	s	54	s	s	s	s	s	s	s	s
27	27	29	41	38	36	26	30	26	19	21	23
28	23	28	39	87	89	54	80	93	49	100	98
29	31	24	61	57	50	52	43	37	32	32	42
31	7	14	17	14	15	12	15	15	9	12	15
32	s	s	s	20	21	12	19	21	10	23	24
39	15	17	37	30	32	21	25	22	14	16	18
41	44	48	100	76	68	68	58	52	45	44	60
42	13	30	35	33	26	17	26	22	15	17	21
43	100	100	83	67	79	38	74	70	47	45	46
44	7	32	22	24	24	14	19	22	14	16	17
45	s	20	12	12	25	13	13	16	9	12	14
54	s	s	21	s	s	s	s	s	s	s	s
55	16	s	76	44	s	58	20	40	34	s	78
56	24	s	85	49	43	52	24	29	27	12	44
57	70	10	10	80	45	100	38	42	43	45	80
59	s	s	s	s	9	s	s	s	s	49	s
70	n	s	10	9	8	16	14	9	11	7	15
71	n	39	72	61	76	87	100	89	100	62	100
73	27	10	8	26	42	51	19	44	33	52	87
85	n	n	31	18	9	32	13	7	15	16	26
86	n	28	n	n	23	n	s	15	n	n	n
87	13	n	8	s	11	12	s	9	n	s	12
100	n	n	22	18	15	20	9	9	9	8	13
101	n	n	37	19	18	n	9	12	13	11	18

s, slight; n, noise.

characteristic of primary alcohol. That is, the peak intensities at $m/Z = 17$ and 31 , are respectively low. IR spectra of POTMG preheated show the presence of considerable amounts of aldehydes as mentioned in the section below. If the major products are a series of compounds with a formyl end and/or a methyl end, they should be fragmented to radical cations with $m/Z = 29, 43, 57, 71, 73, 87, 101, 115$, or/and, etc. (Chart 1) by electron bombardment in a mass spectrometer. Table III suggests that the mass spectra of products 10–21 are products formed by the series of this fragmentation.

A relatively smaller amount of tetrahydrofuran (product 7) was evolved from thermally decomposed POTMG, compared with evolution of ethylene oxide in the thermal decomposition of poly(ethylene oxide).¹⁴ This may be explained in

**Chart 1**

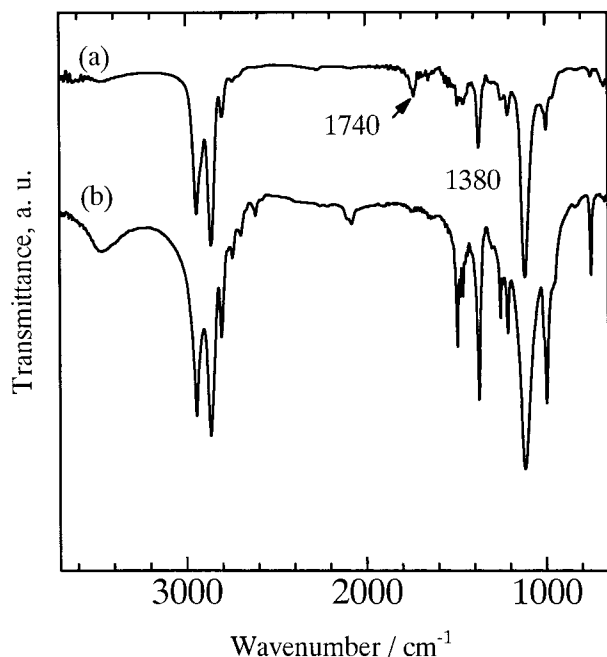


Figure 2 IR spectra of POTMG: (a) preheated at 523°K for 10 min, (b) unpreheated.

terms of the larger molecular motion (deformation) required for the liberation of tetrahydrofuran from POTMG, compared with the smaller molecular motion (distortion) required for the liberation of ethylene oxide from poly(ethylene oxide).

Onset Temperature

Figure 2 shows IR spectra of a preheated sample at 523°K for 10 min and virgin POTMG samples. In the spectrum of the preheated sample, an absorption due to stretching vibration of carbonyl at 1740 cm^{-1} , which is absent in the spectrum of virgin one. In Table IV, the ratios of optical density, OD, of the absorption at 1740 cm^{-1} to OD of the absorption due to the bending vibration of

Table IV $\text{OD}_{1740}/\text{OD}_{1380}$ for POTMG Preheated at Various Temperatures in Nitrogen Gas Flow

Preheating Temperature (K)	$\text{OD}_{1740}/\text{OD}_{1380}$
423	0.01
443	0.43
463	0.41
473	0.45
483	0.41

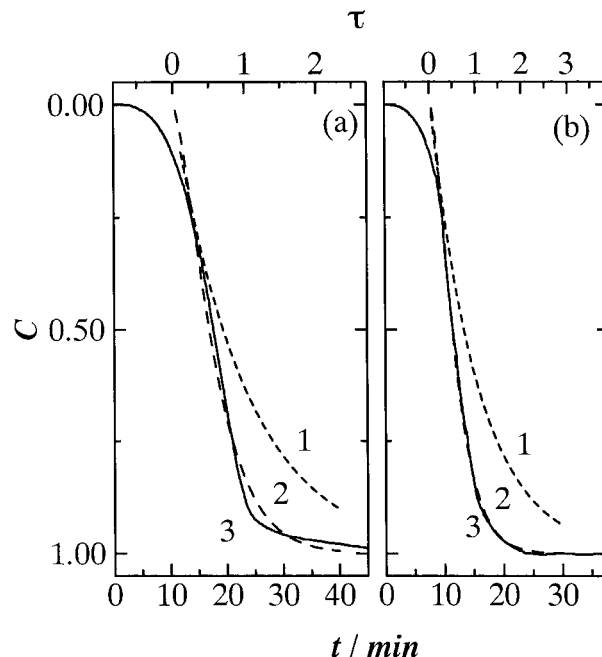


Figure 3 Isothermal TG curves at 483°K (a) and 498°K (b): 1, first order decomposition curves; 2, random decomposition curves ($L = 4$); 3, observed curves.

methylene at 1380 cm^{-1} , $\text{OD}_{1740}/\text{OD}_{1380}$, are shown for the samples heated at various temperatures. Because an increase in $\text{OD}_{1740}/\text{OD}_{1380}$ means an increase in the amount of carbonyl, Table IV suggests that the ether cleavage occurs already at 443°K. In an isothermal TG run at 473°K, 45 wt % mass loss was observed two days after the start of run.

Random Decomposition

In the thermal decomposition of POTMG, many species of products evolve and the initiation temperature of ether cleavage differs from that of vaporization. These are observed in the random thermal decomposition of polymers. Fitting the isothermal TGA curves to the following first-order and random decomposition curves¹⁵ seems to give a similarity of the POTMG thermal decomposition to the random decomposition (see Fig. 3): $dC/d\tau = (1 - C)$ for the first-order decomposition, and $dC/d\tau = (L - 1)(1 - C) - [(N - L)(L - 1)/N]\exp(-L\tau)$ for the random decomposition, where $\tau = kt$, $N = 40$, k is the rate constant, t is the time, C is the conversion equal to unity minus the mass loss, and $(L - 1)$ is the degree of polymerization of the largest evaporated compound. The E_a value equal to 61.6 kJ mol^{-1} is derived from the Arrhe-

Table V The Values of E_a and n Obtained by the Isoconversion Method

Preheating Temperature (K)		Weight (%)				
		90	70	50	30	10
353	E_a/kJmol^{-1}	144–81	130–84	117–81	101–81	98–78
	n	0.99	0.99	0.98	1.00	1.00
363	E_a/kJmol^{-1}	183–93	180–120	183–98	16699	148–98
	n	0.97	0.98	0.98	0.99	1.00
373	E_a/kJmol^{-1}	47–45	56–48	60–53	60–52	63–52
	n	0.98	0.98	0.98	0.98	0.97

The activation energies, E_a , and the orders of reaction, n , are represented by the minimum-to-maximum ranges and the mean of the triplicated data, respectively.

nius relation with the obtained k values ($k = 0.0787 \text{ min}^{-1}$ for 483°K, $k = 0.125 \text{ min}^{-1}$ for 498°K).

Thermally Controlled TGA Results

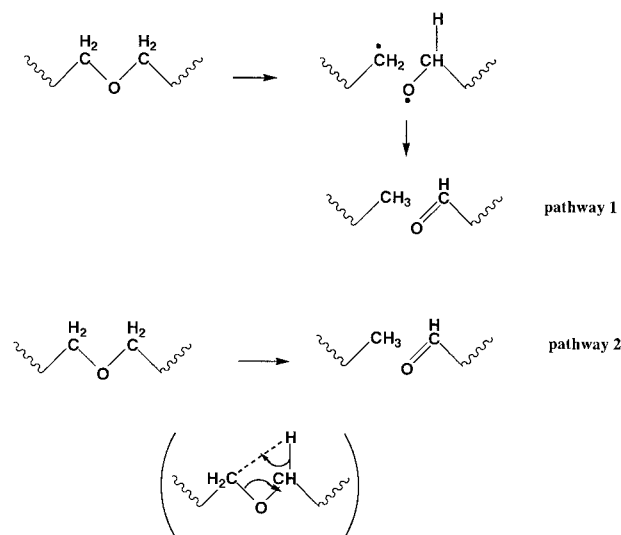
Table V shows the activation energies, E_a , and the orders of reaction, n , determined from the TGA curves obtained at various heating rates. With increasing preheating temperature, the E_a values decline and converge to the E_a value determined from the isothermal TGA data. The E_a values, though scattered even in the runs conducted after the isothermal runs at 373°K, coincide in the order of magnitude with the value in the literature,¹⁶ and are lower than the E_a values of typical thermal decomposition reactions of polymers.

There is no considerable difference in TGA data between POTMG samples with and without a radical capture (onset temperatures of the samples with and without hydroquinone are 342 ± 4 and 341 ± 5 °K, respectively, and the offset temperatures are 399 ± 1 and 400 ± 1 °K, respectively).

Pathway of the Ether Cleavage

The major reaction in thermal decomposition of POTMG is an ether cleavage reaction which gives oligomers with a formyl end and/or a methyl end. Thermal reactions proceed principally by a radical pathway. Therefore, a possible pathway for the ether cleavage is a radical scission of an ether bond, accompanied by transference of β -hydrogen of the oxygen chain end to the carbon another chain end (pathway 1). However, the present article presents some unfavorable evidences for the radical reactions: The activation energy (approx-

imately 62 kJ mol^{-1}) is much lower than the dissociation energy of oxygen-carbon single bond (approximately 320 kJ mol^{-1}). There is no evolution of primary alcohol formed by transfer of β -hydrogen of the carbon chain end to the oxygen of another chain end, and no difference in onset and offset temperatures between POTMG with and without a radical capture, within experimental errors. Nonradical thermal decomposition pathways have been proposed for some polymers, though the pathways are still in doubt: For example, reactions of intramolecular elimination from a substituent for poly(vinyl chloride),¹⁷ poly(vinyl acetate),¹⁸ nonlinear alkyl esters of methacrylic acid,^{19,20} poly(γ -methyl-L-glutamate),²¹ etc., and intramolecular elimination of a unit of main chain for poly(ϵ -caprolactam),²² poly(isocyanate)s,²³ poly(4-hydroxybutyrate),²⁴ poly(β -hydroxybutyrate),²⁵

**Scheme 1**

etc. Herein, we propose a nonradical concerted reaction through a four-membered ring transition state (pathway 2), by consideration of the above three evidences favorable for nonradical reaction.

CONCLUSIONS

The major volatile products of POTMG have been confirmed to be a series of molecules made up by the repetition of oxytetramethylene with formyl and/or methyl ends from the mass spectra. This suggests that the major reaction is a cleavage of ether bond to methyl and formyl ends. This is supported by existence of formyl in the pyrolysis residues, confirmed from the IR spectra. The Simha rate equation for the random decomposition of polymers fit well to the isothermal TGA curves. These evidence that the thermal decomposition proceeds by random ether cleavage. Two pathways have been proposed for the ether cleavage: a radical scission, accompanied by β -hydrogen transfer (pathway 1) and a nonradical reaction through a four-membered ring transition state (pathway 2). The present work presents evidences favorable for pathway 2.

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