KINETIC AND THERMAL STABILITY STUDIES OF BISPHENOL-C DERIVATIVES

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Thermal study of some novel bisphenol-C derivatives has been investigated using TG and DSC techniques under nitrogen atmosphere at the heating rate of 10 ºC min^{-1}. The nature and position of the substituents affect DSC transition, thermal stability, and kinetic parameters. Melting transitions (57-237 ^oC) and heat of fusion (15-78 kJ mol^{-1}) of the compounds have been determined from DSC curves. Bisphenol-C derivatives are thermally stable up to about 215-350 ºC and followed either integral or fractional order degradation kinetics due to structural dissimilarity—different magnitudes of n, E_a and A suggested different degradation mechanisms. Large and negative magnitudes of ΔS^* confirmed a highly ordered transition state, while large and positive magnitudes of ΔS^* confirmed a less ordered transition state.
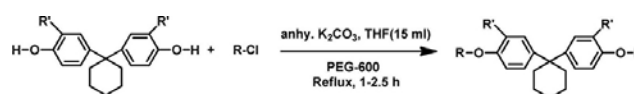
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INTRODUCTION

Bisphenols are important constituents in the polymer and plastic industries.[1-3] Some of them display antibacterial, antifungal, antiviral and estrogenic activity.[4-6] The study of the thermal behavior of the compounds has great potential and is used as a quick and reliable technique for studying purity, crystallinity, thermal stability, glass transition, and polymorphism evaluation.[7-11] Moreover, thermal behavior is an important tool that should be realized before testing the final formulation because biological studies carried on potentially bioactive molecules involve their utilization as different mixtures and rarely as pure compounds. Studies on thermodynamics, mechanism and kinetics of solid-state reactions are a challenging and difficult task with complexity resulting from the great variety of factors with diverse effects such as the reconstruction of the solid-state crystal lattice, formation and growth of new crystallization nuclei, diffusion of gaseous reagents or reaction products, etc.[12-13] Thermal analysis is most widely used for scientific and practical purposes because they provide reliable information on the physicochemical parameters characterizing the processes of isothermal and non-isothermal decomposition.[14] Also, kinetic parameters such as activation energy, pre-exponential factor, and reaction order can be measured by thermoanalytical methods according to reactions' progress.[15] In this paper, we have studied the effect of substituents on the thermal behavior of bisphenol-C derivatives.

EXPERIMENTAL

The sample used in this work were synthesized in laboratory.[16]

Measurements

Differential scanning calorimetric (DSC) curves of the compounds were recorded on a Shimadzu DSC60 calorimeter in nitrogen atmosphere with a flow rate of 50 mL min^{-1}. About 2-3 mg samples were accurately measured, enclosed in an aluminum DSC crucible using crimper, and immediately subjected to a temperature scan from 25 to 250 ºC with an empty aluminum crucible as the reference. Thermogravimetric (TG) curves of the compounds were recorded on a Shimadzu DTG-60H in nitrogen atmosphere with a flow rate of 50 ml min^{-1}. About 3-6 mg samples were put into open alumina pan and subjected to a temperature scan from room temperature to 800 ºC with an empty alumina pan as the reference. The heating rate for all these experiments was fixed at 10 ºC min^{-1}. Indium and zinc metals (99.9 %) were used for the calibration of instruments.

Kinetic analysis

There are several approaches for modeling the complex decomposition process. The simplest is the empirical model, which employs global kinetics, where the Arrhenius expression is used to correlate the rates of mass loss with temperature.

The general expression for the decomposition of a solid sample is

$$\frac{dc}{dt} = kf(c) \qquad \text{A.1}$$

where

    c = degree of conversion,

    t = time,

    k = rate constant,

    $f(c)$ = temperature independent function of c.

The constant k is generally assumed to have the Arrhenius form

$$k = Ae^{E_a/RT} \qquad \text{A.2}$$

c is defined as the conversion with respect to initial material

$$c = 1 - \frac{w}{w_0} \qquad \text{A.3}$$

where

    w_0 = initial weight of the material and

    w = weight of the material at any time.

The residual weight fraction is given by

$$\frac{w}{w_0} = 1 - c \qquad \text{A.4}$$

and the rate of conversions is given by

$$\frac{dc}{dt} = -\left(\frac{1}{w_0}\right)\frac{dw}{dt} \qquad \text{A.5}$$

For homogeneous kinetics, the conversion would be assumed to have the form

$$f(c) = (1-c)^n \qquad \text{A.6}$$

where n = order of the reaction.

Upon substituting Eqns. A.2 and A.6 into Eq. A.1

$$\frac{dc}{dt} = Ae^{-E_a/RT}(1-c)^n \qquad \text{A.7}$$

or

$$\frac{dc}{dt} = \frac{A}{\beta}e^{-E_a/RT}(1-c)^n$$

where β = rate of heating.

Eq. A.7 represents the differential form of the non-isothermal rate law. In this study, the data from non-isothermal experiments are considered to calculate kinetic parameters based on the Anderson-Freeman method to analyze and investigate the thermal behavior of bisphenol derivatives.

Freeman – Carroll and Anderson-Freeman method[17-18]

Freeman-Carroll developed the following relation to analyzing TGA data at a single heating rate:

$$\frac{\Delta \ln(dc/dt)}{\Delta \ln(1-c)} = n - \frac{E_a}{RT}\left[\frac{\Delta \ln(1/T)}{\Delta(1-c)}\right] \qquad \text{B.1}$$

An LHS plot against $\Delta ln\ (1/T)/\Delta\ln(1-c)$ would yield a straight line with a slope equal to $-E_a/RT$ and the intercept equal to n.

Using Eq. B.1, Anderson-Freeman derived Eq. (B.2):

$$\Delta \ln \frac{dw}{dt} = n\Delta \ln w - \left(\frac{E_a}{RT}\right)\Delta\left(\frac{1}{T}\right) \qquad \text{B.2}$$

A plot of $\Delta \ln dw/dt$ against $\Delta \ln w$ for equal intervals of $\Delta(1/T)$ would be a straight line with a slope equal to n and the intercept equal to $-E_a/RT$.

RESULTS AND DISCUSSION

DSC analysis

DSC curves of BC-1 to BC-7 and MEBC-1 to MEBC-7 at 10°C min⁻¹ heating rate under nitrogen atmosphere are presented in Figures 1 and 2, respectively. The melting transitions (T_m) along with the heat of fusion (ΔH) and entropy of transitions (ΔS) are listed in Table 1.

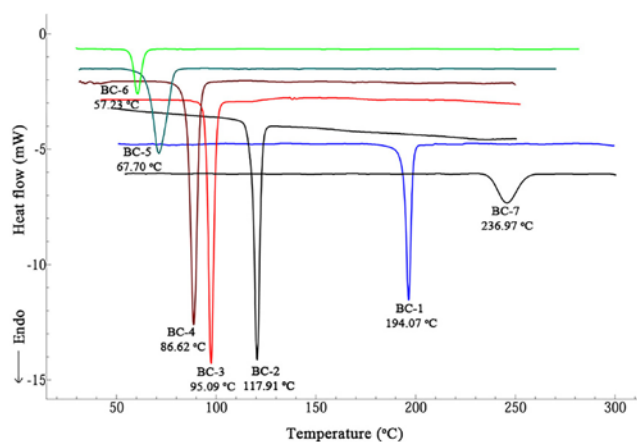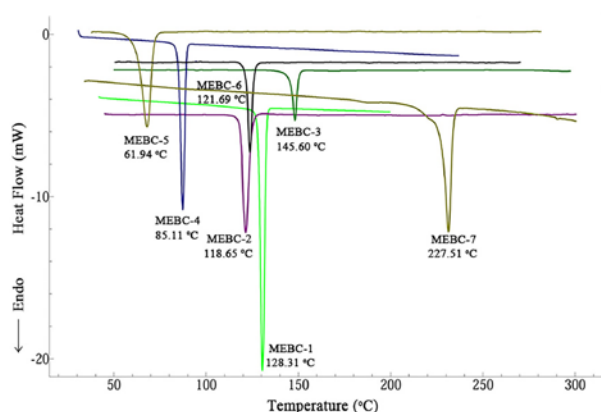**Figure 1.** DSC curves of BC derivatives at 10 ºC min⁻¹ heating rate in nitrogen atmosphere
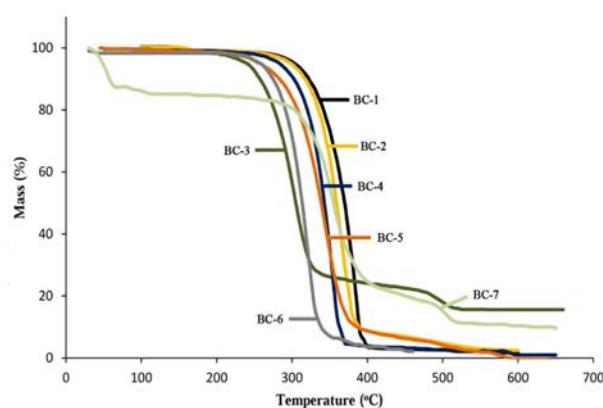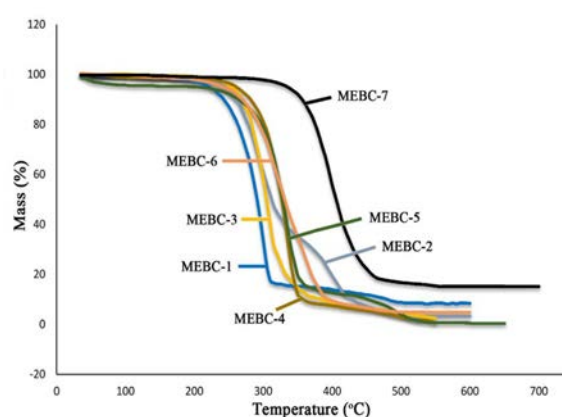
Table 1. DSC data of bisphenol-C derivatives

Compounds	Melting transitions, T_m, °C	The heat of fusion, ΔH, J g^{-1}	ΔH, kJ mol^{-1}	The entropy of transition, ΔS, J K^{-1} mol^{-1}
BC-1	194.07	77.73	34.82	74.53
BC-2	117.91	95.57	37.08	94.82
BC-3	95.09	89.67	36.94	100.32
BC-4	85.62	92.74	38.20	106.49
BC-5	67.70	86.46	38.04	111.26
BC-6	57.23	33.49	15.67	47.44
BC-7	236.97	33.76	16.74	32.82
MEBC-1	128.31	164.13	78.12	194.60
MEBC-2	118.65	102.86	42.37	108.16
MEBC-3	145.60	57.43	25.26	60.34
MEBC-4	85.11	154.38	67.92	189.60
MEBC-5	61.94	86.63	40.41	120.61
MEBC-6	121.69	49.76	24.68	62.52
MEBC-7	227.51	90.58	47.46	94.80

Figure 2. DSC curves of MEBC derivatives at 10 °C min^{-1} heating rate in nitrogen atmosphere

Figure 3. TG curves of BC derivatives at 10 °C min^{-1} heating rate in nitrogen atmosphere

BC-1 showed comparatively high T_m than that of MEBC-1 due to the structural dissimilarity of these two derivatives. BC-1 is a symmetric molecule, while MEBC-1 is an asymmetric molecule and hence packing density will also be different. BC-2 showed more T_m than that of BC-3 because of the difference in flexibility, while the reverse is observed in MEBC-2 and MEBC-3. In the case of alkyl ester of BC, it is observed that T_m decreased up to three carbon atom chain length and beyond this, it caused an abrupt increase in T_m due to restricted free rotation. If MEBC alkyl esters T_m decreased up to two carbon chain length and beyond this, it is increased abruptly. Thus, observed behavior proved that symmetric molecules possess high melting points than those of asymmetric molecules. Restricted free rotation also affects the melting point of the material. The entropy of the compound strongly depends upon heat of fusion and melting point. The ultimate magnitude of ΔS is decided based on the magnitudes of ΔH and T_m.

TG analysis

TG curves of BC-1 to BC-7 and MEBC-1 to MEBC-7 at 10 °C min^{-1} heating rate under nitrogen atmosphere are presented in Figures 3 and 4, respectively.

Figure 4. TG curves of MEBC derivatives at 10 °C min^{-1} heating rate in nitrogen atmosphere

From these figures, it is observed that bisphenols-C derivatives are thermally stable up to about 215-350 °C and followed either single-step decomposition (BC-1, BC-2, BC-4, BC-5, BC-6, MEBC-1, MEBC-3, MEBC-4, MEBC-6 and MEBC-7) or two-step decomposition (BC-3, BC-7,

MEBC-2 and MEBC-5). Various characteristic temperatures such as initial decomposition temperature (T_0), temperature of 10 % mass loss (T_{10}), decomposition range, temperature of maximum mass loss (T_{max}), % mass loss involved in each step and % residue left at the end of the decomposition reaction are reported in Table 2. BC-1 (325 °C) showed higher thermal stability than that of MEBC-1 (215 °C) due to the compounds' structural dissimilarity. BC-2 (325 °C) showed considerably high thermal stability than BC-3 (255 °C). The observed difference in thermal stability is due to the more rigid nature of BC-2. MEBC-3 (270 °C) showed somewhat higher thermal stability than MEBC-2 (260 °C), which is due to the more rigid nature of MEBC-3. BC-4 (295 °C) and BC-5 (295 °C) showed identical thermal stability, while BC-6 (285 °C) showed somewhat low

thermal stability due to the increased flexibility of the ester molecule. BC-7 (320 °C) showed improved thermal stability due to increasing rigidity. Thermal stability is found to decrease as carbon chain length increased in MEBC-4 (295 °C) to MEBC-5 (285 °C) to MEBC-6 (260 °C). Again, thermal stability is improved in the case of MEBC-7 (350 °C) due to the increasing rigidity of this ester. Up to three carbon chain length- thermal stability is found to decrease, but it caused increased thermal stability. Thus, the structure of BC derivatives played an important role in their thermal stability. Similar trends are also observed for T_{10} and T_{max}. BC-3, BC-7, MEBC-1 and MEBC-7 showed a considerable residue at 600 °C and others are practically decomposed to small hydrocarbons.

Table 2. TGA data of bisphenol-C derivatives

Compounds	T_0, °C	T_{10}, °C	T_{max}, °C	Decomp. Range, °C	Mass loss, %	Residue at 600 °C, %
BC-1	325	343	377.25	325-400	85.28	1.64
BC-2	325	347	363.79	325-390	76.81	2.43
BC-3	255	275	302.38	255-330	62.25	16.0
	460	-	496.60	460-525	6.41	-
BC-4	295	317	363.79	295-375	87.71	1.0
BC-5	295	313	342.23	295-380	74.93	0.3
BC-6	285	296	317.69	285-340	75.27	2.3
BC-7	320	339	352.82	320-390	47.67	10.4
MEBC-1	215	252	289.43	215-310	78.36	8.4
MEBC-2	260	278	295.25	260-335	89.95	3.4
	380	-	398.17	380-435	18.95	-
MEBC-3	270	283	301.56	270-335	69.94	2.5
MEBC-4	295	308	331.99	295-335	73.59	-
MEBC-5	285	305	330.16	285-365	69.86	0.6
	465	-	493.40	465-535	7.76	-
MEBC-6	250	286	332.19	250-400	84.59	5.0
MEBC-7	350	372	274.04	350-450	69.86	15.2

Kinetic analysis

The associated kinetic parameters such as the energy of activation (E_a), frequency factor (A), order of the reaction (n) and entropy change (ΔS^*) for all compounds were derived from using Eq. B.2.

$$A = \frac{E_a \beta}{RT^2} e^{(E_a/RT)} \qquad \text{B.3}$$

$$\Delta S^* = R \ln Ah/kT \qquad \text{B.4}$$

where

    β is the heating rate,

    R is the gas constant,

 h is the Planck's constant,

    T is temperature and

    k is the Boltzmann constant.

The least-square values of the parameters mentioned above, along with regression coefficients (R^2), are reported in Table 3. The entropy change ΔS^* was determined at corresponding T_{max}.

From Table 3, it is observed that BC-1 followed first order (0.8) degradation kinetics, while MEBC-1 followed second-order (1.8) degradation kinetics. BC-2 followed fractional order (0.6) kinetics, while MEBC-2 followed two steps each of apparently first-order (1.1) degradation kinetics. BC-3 followed two steps, each of apparently first-order (0.9 and 1.0) degradation kinetics, while MEBC-3 followed single step second-order (2.0) degradation kinetics. BC-4 followed one-half order (0.5) degradation kinetics, while MEBC-4 followed first order (1.1) kinetics. BC-5 followed first order (1.4) kinetics, while MEBC-5 followed two steps each of one-half order (0.6) and apparently first-order (1.3) kinetics, respectively. Both BC-6 and MEBC-6 followed apparently first order (0.9 and 1.2) kinetics. BC-7 followed apparently second-order (1.9) kinetics, while MEBC-7 followed first (1.1) kinetics. Thus, the structural dissimilarity between BC and MEBC derivatives caused different degradation mechanisms.

Table 3. The kinetic parameters of bisphenols-C derivatives derived according to the Anderson-Freeman method

Compounds	n	E_a, kJ mol^{-1}	A, s^{-1}	ΔS^*, J K^{-1} mol^{-1}	R^2
BC-1	0.8	166.28	1.78×10^{11}	-36.01	0.998
BC-2	0.6	155.39	1.65×10^{7}	-113.01	0.993
BC-3	0.9	109.74	6.0×10^{7}	-101.39	0.998
	1.0	276.02	5.65×10^{16}	67.92	0.971
BC-4	0.5	209.18	1.47×10^{15}	39.17	0.998
BC-5	1.4	156.30	1.53×10^{11}	-36.81	0.981
BC-6	0.9	165.61	4.17×10^{12}	-9.00	0.991
BC-7	1.9	221.15	3.22×10^{16}	64.94	0.989
MEBC-1	1.8	145.66	3.08×10^{11}	-30.24	0.999
MEBC-2	1.1	110.74	1.03×10^{8}	-96.86	0.975
	1.1	169.14	1.09×10^{11}	-40.36	0.976
MEBC-3	2.0	240.10	6.69×10^{19}	132.25	0.985
MEBC-4	1.1	180.24	3.57×10^{13}	8.65	0.993
MEBC-5	0.6	80.47	4.11×10^{4}	-162.43	0.990
	1.3	255.73	2.33×10^{15}	41.42	0.992
MEBC-6	1.2	67.84	2.60×10^{4}	-185.42	0.998
MEBC-7	1.1	156.30	8.71×10^{12}	-2.23	0.980
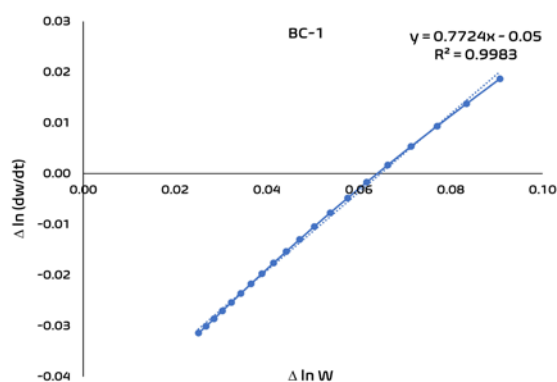
Figure 5. The Anderson-Freeman plot of BC-1
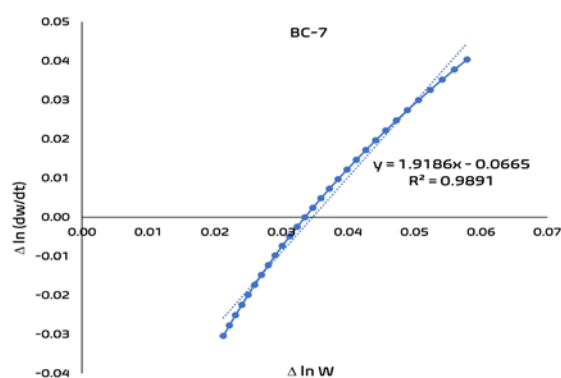
Figure 7. The Anderson-Freeman plot of BC-7
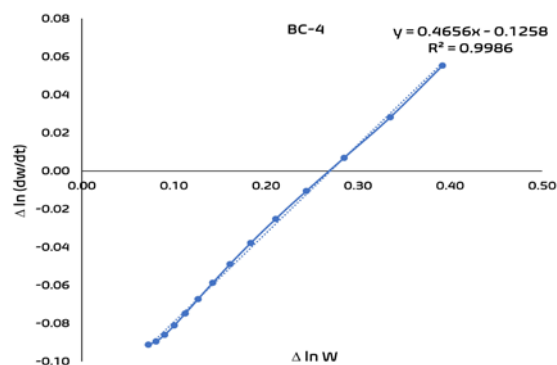
Figure 6. The Anderson-Freeman plot of BC-4
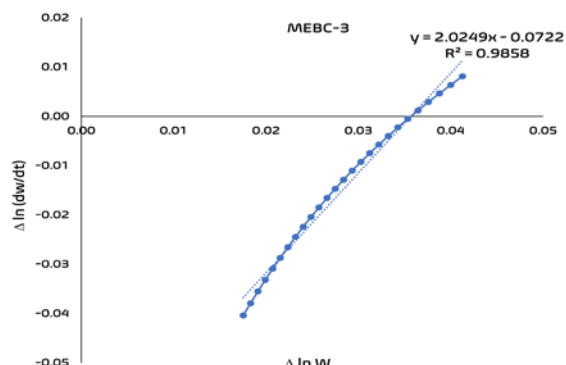
Figure 8. The Anderson-Freeman plot of MEBC-3

Depending upon structure and molecular flexibility, BC and MEBC derivatives showed different magnitudes *Ea* and *A*. The more rigid is the molecule, the higher values of *Ea* and *A* were found. Symmetric molecules (BC-1 to BC-7) showed higher E_a and *A* magnitudes than asymmetric molecules (MEBC-1 to MEBC-7). Carbon chain length in the ester molecules also affected E_a and *A*.

A large and negative magnitude of ΔS^* suggested that the transition state is in a more orderly state than that of BC/MEBC, while a large and positive magnitude of ΔS^* suggested that transition is more in a disorderly state. Degradation of the compounds is complex and involves various relations such as cleavage, rearrangement, branching, cross-linking, etc.
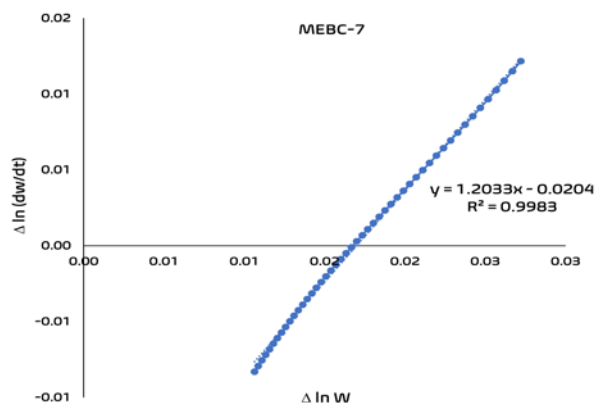
Figure 9. The Anderson-Freeman plot of MEBC-6

Methyl side substituent in MEBC, ether and ester linkages are weak linkages so selective degradation starts from such junction with the evaluation of hydrocarbon gases and formation of free radicals, which further undergo secondary reactions to form new compounds and degrade at elevated temperatures.

A considerable amount of residue left at 600 °C for BC-3 (16 %), BC-7 (10.4 %), MEBC-1 (8.4 %) and MEBC-7 (15.2 %) suggested formation of highly thermally stable compounds. Other compounds are practically decomposed into low molecular mass hydrocarbons. Thus, different molecular structures and nature showed different thermal behavior and degradation kinetics.

CONCLUSIONS

The thermal behavior of bisphenol-C derivatives is affected both by molecular symmetry and the nature of the compounds. Bisphenol-C derivatives followed either fractional or integral order of degradation kinetics supporting different degradation mechanisms.

ACKNOWLEDGMENTS

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