

Thermal Degradation Kinetics of Polyesters Containing Mesogenic Aromatic Diols

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ABSTRACT: A series of polyesters were synthesized by reacting structurally differing aromatic diols with either saturated (flexible) or unsaturated (rigid) dicarboxylic acid halide by a stirred interfacial polycondensation technique. Thermal degradation kinetics of these polyesters were investigated by applying Coats–Redfern and Horowitz–Metzger nonisothermal procedures. The dynamic thermogravimetry experiments were conducted in nitrogen to obtain differential thermogravimetric plots. Thermal stability of these polyesters was discussed on the basis of semiquantitative methods such as differential procedural decomposition temperature, integral procedural decomposition tem-

perature, and fraction decomposition temperature (e.g., 10% DT). Degradation proceeded in multiple stages. The thermal degradation patterns and activation energies in these stages were discussed in relation to central bridging moieties of aromatic diol. The activation energies of these polyesters were found to be in the range of 100 to 200 kJ/mol. The effect of spacer type on activation energy was also reported. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 784–792, 2005

Key words: degradation; activation energy; polycondensation; kinetics (polym.); polyesters

INTRODUCTION

Liquid crystal (LC) polymers are used increasingly worldwide as special materials with good mechanical properties such as modulus strength. However, properties related to orientation decrease substantially as a result of anisotropy. To overcome this problem, the introduction of reactive double bond into the polymer chain had a positive effect. Thermoplastics and thermosets could be transformed into liquid crystal compounds by incorporating mesogenic units to generate an unusual combination of properties.^{1,2} Introduction of fumaroyl units into the flexible spacer of liquid crystal polymers allows a structure-fixing crosslinking reaction. Thus, unsaturated polyesters with liquid crystal elements can be synthesized by incorporating a combination of rigid mesogenic units with the semiflexible fumarate units along the chain to fix the LC state. For this purpose it is important to know the thermal stability of the polymer. Similarly, thermal degradation kinetics of the polyesters help to establish a relation between thermal degradation behavior with the structural variances such as changes in aromatic moieties and spacer type. Possible applications of liquid crystal thermosets include advanced adhesives,

new matrix materials for composites, and a variety of applications for the microelectronics industry. These compounds have also been studied as optical materials and polarizers. The available literature on unsaturated polyesters describes maleates quite extensively, although reports on fumarates are rather limited. The typical functional crosslinkable units in the main chain are cinnamoyl, *p*-phenylene, diacryl, or stilbene. Functional end units used have been maleimide, epoxy, vinyl, isocyanate, acetylene, or acrylate.^{3–5}

Dialkyl fumarate polymerizes radically to produce high molar mass non- or semiflexible rodlike polymers.^{6,7} Sugiyama⁸ synthesized liquid crystalline polymers from fumarates containing mesogenic methoxyphenyl azophenoxy groups and showed that, when bound directly to the polymerizable group, an enantiotropic nematic phase was noted, but when bound to the vinylene group by a spacer, the mesophasic character of the monomer disappears as a result of the dilution effect. Replacement of flexible saturated aliphatic spacer with rigid fumaroyl unit depresses the mesogenicity.⁹ Devar and Riddle¹⁰ observed a substantial destabilization of mesophase when R in Figure 1 was a fumaroyl unit.

The cause for this was interpreted to be the result of a local decrease in thickness ascribed to the waist formation arising from the presence of a fumaroyl unit. The rodlike molecules of liquid crystalline compound should have the same cross section along the

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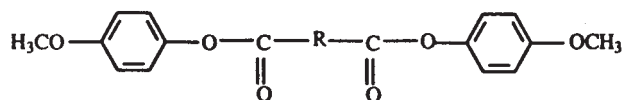


Figure 1 Bis-(4,4'-dimethoxy)-fumarate.

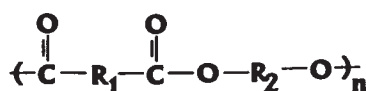
entire length. Because the bonds in the fumaroyl unit are not coaxial, this compound can exist as two conformers, differing in anisometry. Fradet et al.¹¹ investigated the crosslinking of polyesters with a fumaroyl unit. Poly(2-methyl-1,4-phenylene-fumarate) and poly(2-methyl-1,4-phenylene fumarate)-*block*-poly(alkylene fumarate/adipate) were synthesized and crosslinking was investigated using infrared spectrophotometry. The =CH out-of-plane absorption of fumarate group occurs near 975 cm^{-1} and that for the CH=CH group are observed at 900 and 975 cm^{-1} , depending on the structural differences in polyesters.¹² M. Abd El-Wahab¹³ studied the nonisothermal decomposition of six unsaturated polyesters by thermogravimetry (TG) in air and reported that the decomposition of these polymers proceeds in four stages.

In the present study, thermal stabilities of a series of polyesters synthesized by reacting structurally differing aromatic diols with either saturated (flexible) or

unsaturated (rigid) dicarboxylic acid halide were analyzed by TG. Thermal degradation kinetics of these polyesters were investigated by applying nonisothermal procedures. Thermal stability of these polyesters are discussed on the basis of semiquantitative methods such as differential procedural decomposition temperature (dpdt), integral procedural decomposition temperature (ipdt), and fraction decomposition temperature (e.g., 10% DT). The ipdt temperatures of synthesized polyesters are matched with those of commercially available polymers. Thermal stability of these polyesters is discussed in relation to the central link unit of mesogenic diol as well as the dicarboxylic acid unit.

EXPERIMENTAL

Homopolyesters were synthesized by established procedure¹⁴ by condensing aromatic diols with either sebacoyl or fumaroyl chloride. The reagents used and general structure of homopolyesters are listed in Figure 2. The synthesized polyesters are coded on the basis of diols such as BP for 4,4'-biphenol; AZ for 4,4'-dihydroxyazobenzene; AX for 4,4'-dihydroxyazoxybenzene; DS for 4,4'-dihydroxy diphenyl sulfone; BC for 2,6 Bis (4-hydroxy benzylidene) cyclohexanone



Where R1 = -CH=CH-(fumaroyl) or -(CH₂)₈- (sebacoyl) and list of R₂ is given below

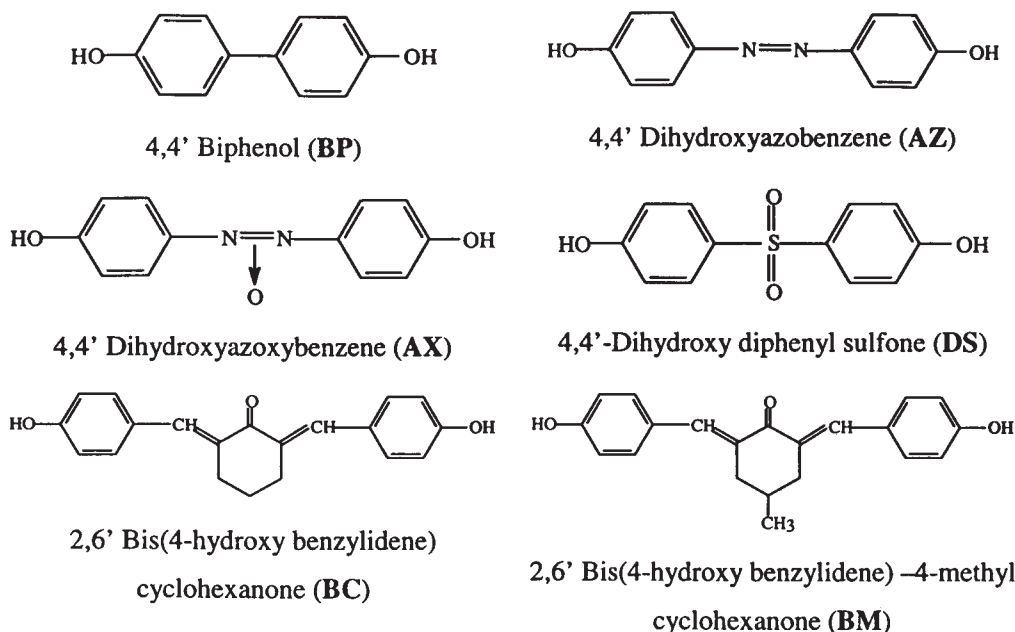


Figure 2 Schematic representation of polyesters.

TABLE I
Procedural Decomposition Temperatures of Polyesters of Fumaroyl/Sebacoyl Chloride and Aromatic Diols

No.	Polymer code	10% DT (K)	25% DT (K)	40% DT (K)	dpdt (K)	ipdt (K)
1	FBP	288.0	327.0	361.9	474.8	384.3
2	FDS	259.1	326.1	358.1	519.6	386.9
3	FAX	264.2	293.0	342.1	539.8	389.3
4	FBM	310.9	351.6	404.7	585.5	433.1
5	FBC	291.3	365.6	404.7	566.7	443.0
6	FAZ	306.3	348.6	510.1	620.7	467.1
7	SBP	361.1	404.9	420.7	483.7	425.8
8	SDS	310.4	351.1	366.6	463.4	376.0
9	SAX	316.2	337.3	387.2	460.6	401.0
10	SBM	379.2	422.2	444.8	553.1	453.5
11	SBC	335.4	420.7	454.4	546.1	448.4
12	SAZ	270.4	295.9	377.1	525.0	386.8

dpdt, differential procedural decomposition temperature; ipdt, integral procedural decomposition temperature.

and BM for 2,6 bis(4-hydroxy benzylidene)-4-methyl cyclohexanone. The letter F was prefixed to the diol designations when the polyesters were based on fumaroyl chloride and S was prefixed to the designations when the polyesters were based on sebacoyl chloride. Details of synthesis of homopolyesters were discussed in a previous report.¹⁴ The polyesters were primarily characterized by IR spectrophotometry, differential scanning calorimetry (DSC), and optical microscopy. Thermal degradation of polyesters was studied in nitrogen using a TA 4000 thermogravimetric analyzer (Mettler Toledo GmbH, Württ, Germany). The approximate sample size taken for analysis was around 10–20 mg. Polyesters were heated at a constant rate of 10°C/min. Thermograms were obtained in the temperature range of 25–900°C.

RESULTS AND DISCUSSION

Structures of polyesters evaluated for thermal degradation kinetics, presented in Figure 2, consist of two series of polyesters based on fumaroyl chloride and sebacoyl chloride. Six different aromatic diols were used to produce six different polyesters in each series. The synthesis strategy of these polyesters is described elsewhere.¹⁴ The TG thermogram of multistage degradation is more complicated because the nature of these thermograms principally depends on the reaction order (n), preexponential factor (A), and the energy of activation (E).¹⁵ The slope of the TG scan at temperature T relates to the rate of degradation. It is quite difficult to calculate the slope in the steep region of the TG trace. These difficulties can be overcome by application of differential thermogravimetric analysis (DTG), where the height of the DTG curve depicts the degradation rate at that temperature. The area under the DTG peak is directly proportional to the extent of weight loss during degradation. The ratio of area under the peak up to temperature T to total area under

the DTG peak gives the value of fractional decomposition (α), which is finally used to determine degradation kinetics. DTG curves not only simplify the estimation of α but also ensure the feasibility in estimation of both initial and final degradation temperatures.¹⁶

Doyle¹⁷ proposed two indices of thermal stability in terms of decomposition temperature: dpdt and ipdt. The nature of a TG scan depends on a number of experimental parameters. Therefore, a semiquantitative ipdt index was devised as a method of adding up the entire shape of the normalized thermogram in the total accessible temperature range (e.g., 25 to 900°C). The dpdt and ipdt temperatures, represented in Table I, were obtained from normalized TG thermograms in the temperature range 25 to 900°C. The ipdt values were calculated from the equation $ipdt = 875A^*K^* + 25$, where A^*K^* represents the comprehensive index of intrinsic thermal stability. Other thermal stability indices have also been reported or designed.¹⁸ These include semiquantitative methods such as 10% DT or tangential temperature (TTN), 25 and 40% degradation (10% DT, 25% DT, 40% DT).

In Table I, polymers with code prefixed by F stand for fumaroyl chloride-based polyesters, whereas S stands for sebacoyl chloride-based polyesters as indicated earlier. The next two letters represents aromatic diols (Fig. 2). The superimposed DTG plots of these polyesters in the range temperature range 25 to 700°C are presented in Figures 3 to 6. The superimposed DTG thermograms of polyesters FBP, FDS, FAZ, and FAX are shown in Figure 3. It is clear from the figure that the degradation of these polyesters shows a multistage pattern, except polyester FAZ, and degradation begins at around 280°C (Fig. 3). A multistage decomposition pattern was observed for polyesters FBP, FDS, and FAX. In FAX the second stage is small and observed as a shoulder, whereas in polyester FDS, the first stage is small

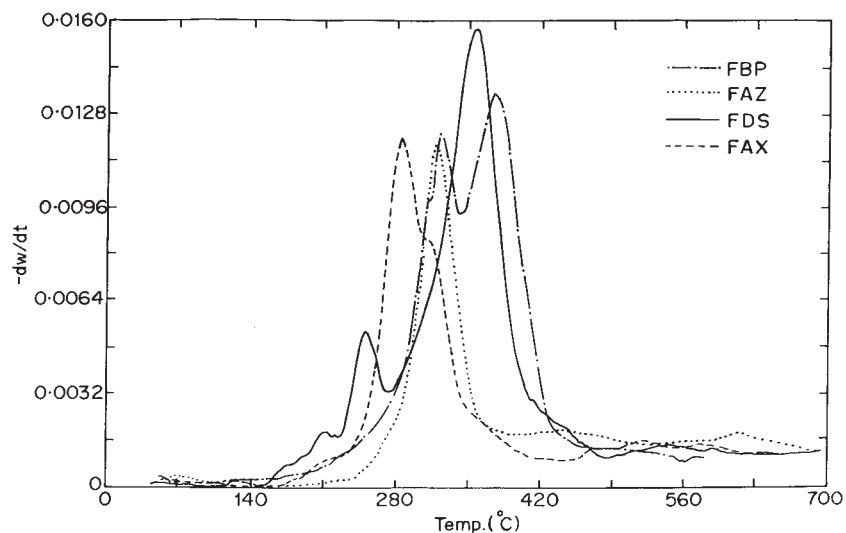


Figure 3 DTG thermogram of polyesters of fumaroyl chloride with BP, DS, AZ, and AX diols.

and appeared as a separate degradation zone. Two notable degradation zones were observed for FBP polyesters as well. A 10% degradation temperature (10% DT) and ipdt range for these polyesters are in the temperature range 260–300°C and around 390°C, respectively. DTG thermograms of polyesters based on fumaroyl chloride with substituted and unsubstituted bis(benzylidene) cyclohexanone diol are presented Figure 4, along with a DTG of FBP polyesters. It is obvious from the figure that bis(benzylidene) cyclohexanone-based polyester follows a two-stage degradation, whereas 4-methyl substituted bis(benzylidene) cyclohexanone polyester indicates a single-stage degradation pattern. This single stage may arise from the overlapping of two closely spaced degradation patterns. A 10% DT and

ipdt for these polyesters are around 300 and 400°C, respectively. These values are higher than those of the polyesters described earlier, and can be attributed to insertion of an additional cyclic ring into aromatic rings instead of heterocentral link units.

DTG thermograms of polyesters of sebacoyl chloride with BP, DS, AZ, and AX diols (SBP, SDS, SAS, and SAZ) are presented in Figure 5. Figure 5 shows multistage decomposition zones for polyesters SAX and SAZ. For SAX polyester, two well-separated degradation zones are observed, whereas SAZ displays a three-stage degradation pattern, with a minor central zone of degradation. Polyesters without a central link unit (e.g., SBP) show single-stage degradation and degrades at high temperature compared to other polyesters.

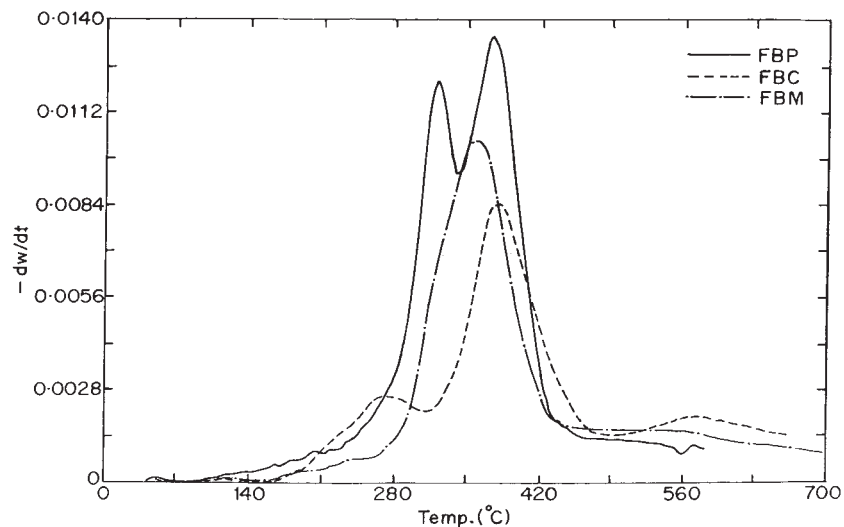


Figure 4 DTG thermogram of polyesters of fumaroyl chloride with BP, BC, and BM diols.

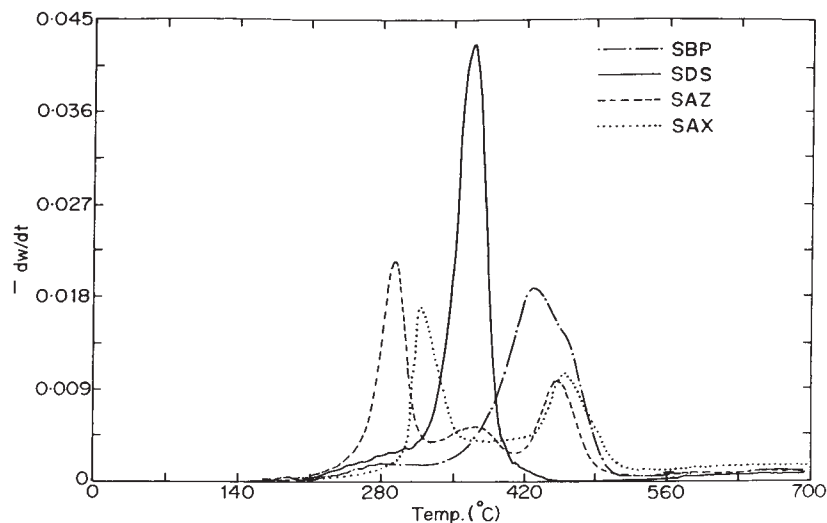


Figure 5 DTG thermogram of polyesters of sebacoyl chloride with BP, DS, AZ, and AX diols.

In this series of polyesters, the degradation starts around 300°C, which is higher than that of the respective fumaroyl chloride-based polyesters. This also reflects on 10% DT data for these polyesters. Sebacoyl moiety-containing polyesters are more thermally stable than respective fumaroyl moiety-containing polyesters, as is evident from their 10% DT data, which is around 40–70°C higher. The 10% DT data for these polyesters are in the range of 270–360°C and dependent on the central link unit of mesogenic diol. A similar trend is observed in its ipdt data; the ipdt value for SBP is 425.8, which is higher than that of SDS, SAZ, and SAX polyesters, in the range of 370–400°C.

Insertion of an additional cyclic unit (as in polyester SBC and SBM) into the polyester backbone increased thermal stability by 25°C, as is apparent from their

ipdt temperatures. The superimposed plots of these polyesters along with polyester SBP are shown in Figure 6, where it is observed that the ipdt values of sebacoyl chloride-containing polyesters are higher than those of the respective fumaroyl chloride-based polyesters (Table I), except polyester FAZ. The polyester of fumaroyl chloride with 4,4'-dihydroxyazobenzene (FAZ) shows the highest ipdt value compared with that of all the other 11 polyesters. This can be attributed to formation of thermally stable amide azomethine links by a possible high-temperature transamidation reaction between C=C of the fumaroyl unit and N=N of the azo diol,¹⁹ which ultimately forms a thermally more stable substituted triazinic structure. Azomethines undergo chemical modification by both addition and condensation reactions at high temperature. The requirements necessary for

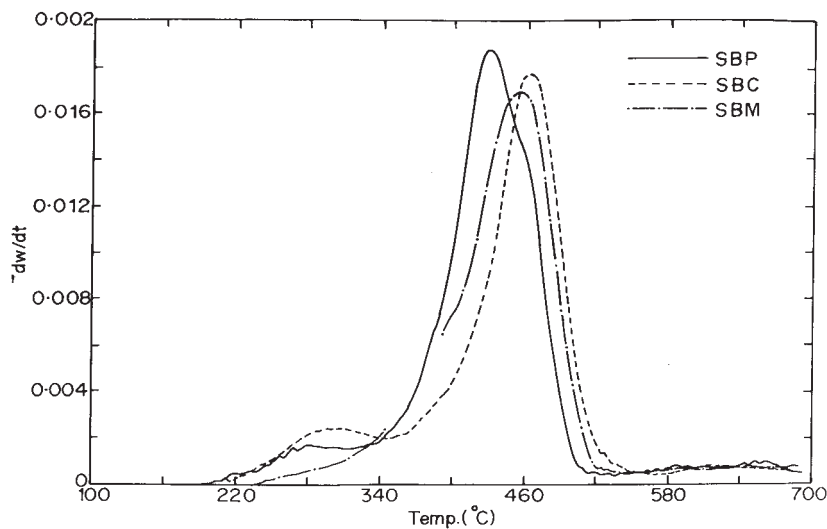


Figure 6 DTG thermogram of polyesters of sebacoyl chloride with BP, BC, and BM diols.

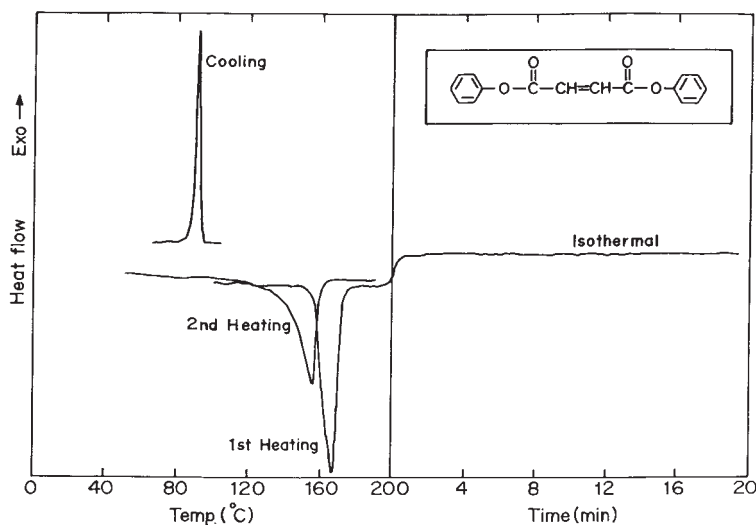


Figure 7 DSC thermogram of 1,2-*trans*-diphenyl fumarate.

triazine structure formation were not present in other polyesters investigated.

Factors such as melting or softening point, bond strength, crosslinking, activation energies, and the presence of low molecular weight volatile materials can affect the thermal stability of polyesters.²⁰ To disclose the mechanism of thermal degradation, it is indispensable to study the high-temperature changes in low molecular weight compounds or model compounds. In the present investigation, we had investigated high-temperature transformations of bis(benzylidene) cyclohexanone diol and model compound 1,2-*trans*-diphenyl fumarate (DPF). These compounds were analyzed by DSC. In this method, compounds were heated above their melting temperature and kept isothermally for 25 min, followed by cooling to room temperature and then

reheated to obtain the respective thermograms. Results of these analysis are represented in Figures 7 and 8. It is obvious from Figure 7 that the T_m of model compound DPF is reduced and shifted to a lower temperature as a result of reduction in crystallinity arising from crosslinking by the fumaroyl unit. In the case of DSC thermogram of bis(benzylidene) cyclohexanone diol (Fig. 8) the T_g was observed around 84.4°C during the second heating, which clearly indicates that the crystallinity of the bis(benzylidene) cyclohexanone diol is totally lost because of the thermal rearrangement of diol.²¹ Thermal transformation in the bis(benzylidene) cyclohexanone system occurs at a higher temperature than that of fumaroyl unit because its T_m (283°C) is almost 100°C higher than the T_m of DPF. The higher ipdt values of sebacoyl-based polyesters can be

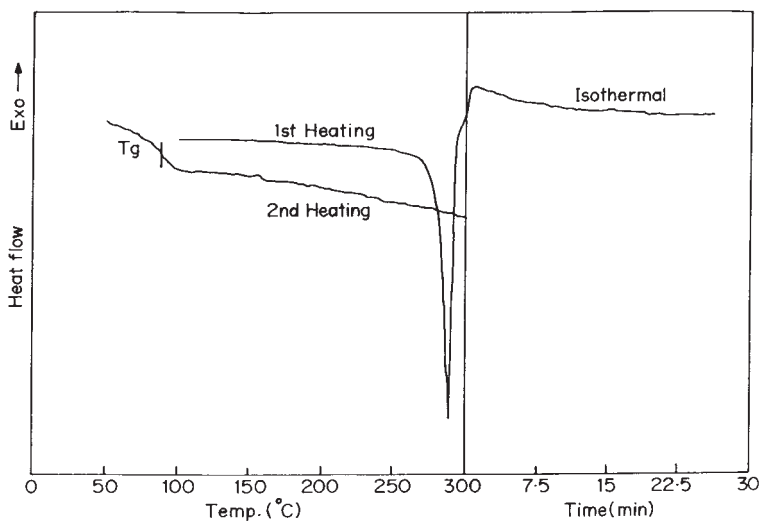


Figure 8 DSC thermogram of 2,6-bis(4-hydroxy benzylidene) cyclohexanone.

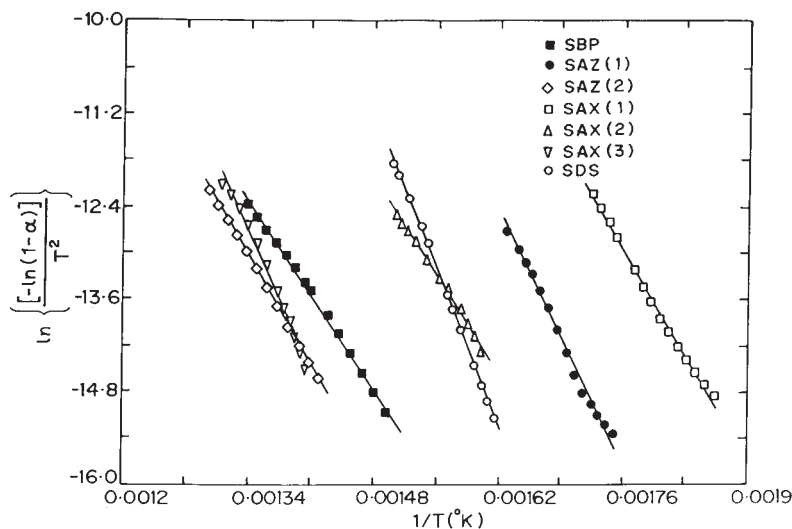


Figure 9 Superimposed Coats-Redfern plots of polyesters of sebacoyl chloride with BP, AZ, and AX diols.

explained on this basis. In both series, bis(benzylidene) cyclohexanone-containing polymer shows a higher thermal stability.

The thermal degradation kinetics of these polyesters was investigated by applying Coats-Redfern and Horowitz-Metzger nonisothermal integral methods.²² The dynamic thermogravimetric experiments were carried out in nitrogen to obtain the DTG plots. The ratio of partially integrated area at temperatures T to the total area was used to estimate the fractional degradation in the analysis. The activation energy of the degradation stage was evaluated. The DTG peak relating to this stage was separated out and corrected for area using Anderson-Freeman methodology.²³ The equations used are the following:

- Coats-Redfern equation I (CR I)

$$\log\{1 - (1 - \alpha)^{1-n}/(1 - n)T^2\} = \log(AR/aE)[1 - (2RT/E)] - E/2.303RT \quad (1)$$

- Coats-Redfern equation I (CR II)

$$\log\{-\ln(1 - \alpha)/T^2\} = \log(AR/aE)[1 - (2RT/E)] - E/2.303RT \quad (2)$$

- Horowitz-Metzger method

$$\ln[-\ln(1 - \alpha)] = E\theta/RT^2s \quad (3)$$

where $\alpha = (W - W_f)/(W_0 - W_f)$, where W_0 , W_f , and W are the initial mass, final mass, and mass remaining at temperature T (equivalent to the final degradation stage); $\theta = T - T_s$, where T_s is the temperature at $W/W_0 = 1/e$. CR II is valid for reactions with order

parameter (n) equal to 1 and CR I is applicable for reactions with order parameters other than 1. Equations CR I and CR II are used to estimate the order of degradation by plotting the function on the left against $1/T$. A correlation coefficient close to 1 describes the order. On this basis, it was found that all these polyesters follow first-order kinetics, which is characteristic of a random chain-scission degradation process with Gaussian distribution.^{24,25}

The energies of activation (E_a) for all the synthesized polyesters were evaluated from the slope of the straight line of the plots of $\ln[-\ln(1 - \alpha)^{-1}/T^2]$ against $1/T$ (CR II). This was further confirmed through the Horowitz-Metzger equation, $\{\ln[-\ln(1 - \alpha)]$ against θ). The correlation coefficients " r " for the plots were also determined in each case. These were found to be near unity for 24 plots, reflecting linearity of the curves. Superimposed plots of $\ln[-\ln(1 - \alpha)^{-1}/T^2]$ against $1/T$ for the degradation stage of the sebacoyl unit-based polyesters are presented in Figures 9 and 10.

Analysis ranges of temperature and percentage decomposition, along with activation energies for different degradation zones obtained from graphs, are tabulated in Table II. The values of E obtained are dependent on the amount of sample decomposed per degree rise in temperature and are highly dependent on melt viscosity. Therefore, in polymer degradation, activation energies are diffusion controlled.²⁶ Homopolyesters with a flexible sebacoyl unit degrade faster. Higher values of E were attributed to low melt viscosity because most of them formed a liquid crystalline phase.¹⁴ Rigidity of spacer and partial crosslinking of polyesters based on fumaroyl chloride at high temperature hinder evolution of degradation products. In the series, the highest values were obtained (Table II) for

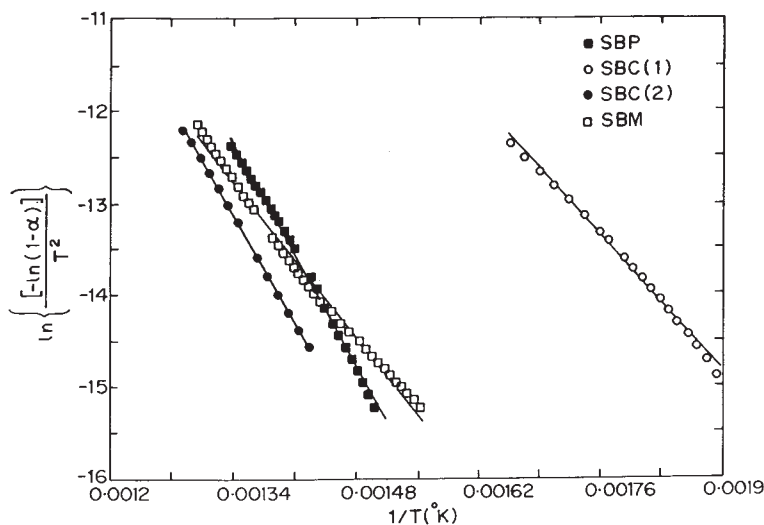


Figure 10 Superimposed Coats-Redfern plots of polyesters of sebacoyl chloride with BP, BC, and BM diols.

polyester based on 4,4'-dihydroxy sulfone and sebacoyl chloride as well as polyester based on 4,4'-dihydroxyazobenzene and sebacoyl chloride. These polyesters have the highest E values. Various methods are discussed in the literature to correlate energy of activation with either 10% DT or sum of 10% DT and ipdt. In Figure 11, the energy of activation (E) is plotted against $1/dT_{(25-55)}$. The value $dT_{(25-55)}$ is the temperature difference between 25 and 55% degradation and the parameter $1/dT_{(25-55)}$ represents the apparent rate of decomposition in the 25 to 55% degradation range. It is evident from the figure that the relationship between E and the semiquantitative parameter $1/dT_{(25-55)}$ is lin-

ear, with slight variance, and has structural dependency. Here, the top line depicts thermally stable sebacoyl-based polyesters, whereas the bottom line represents less-stable fumaroyl unit-containing polyesters. To establish the exact structure-property relationship in degradation kinetics, thermal degradation analysis must be carried out on polymers of identical chain length, given that the rate of chain scission depends primarily on macromolecular chain length.²⁷

CONCLUSIONS

The ipdt values of common commercial polymers range between 400 and 500°C, such as polystyrene, polymethylmethacrylate, polytetrafluoroethylene, Kel F, Viton A, and Silicon resin, for example. Polyesters synthesized in the present study were observed to be in the same range. The thermal stability of polyesters based on sebacoyl chloride is higher than that of those based on fumaroyl chloride. Similarly, the activation energy of polyesters based on sebacoyl chloride is higher than that of those based on fumaroyl chloride, indicating that homopolyester with a flexible sebacoyl spacer degrade faster. Homopolyesters with flexible sebacoyl spacer exhibit liquid crystalline phases and, as a consequence, they have low melt viscosity that results in higher activation energy values. In the case of semiquantitative degradation of 10% DT values, polyester based on bis(benzylidene) cyclohexanone values are higher than those of polyesters based on 4,4'-dihydroxy biphenyl diol. This effect is attributed to the introduction of an additional cyclic ring into aromatic rings. In other cases the central links are not aromatic. In an overall comparison of ipdt values of polyesters, polyesters based on fumaroyl chloride and 4,4'-dihydroxyazobenzene showing higher values

TABLE II
Decomposition Activation Energies of Polyesters of Fumaroyl/Sebacoyl Chloride and Aromatic Diols

Polymer code	Analysis range		E_a (kJ/mol)
	T (K)	% Decomposition	
FBP stage 1	537.4-607.6	10.5-81.4	94.2
stage 2	635.1-697.8	19.8-95.1	138.2
FDS stage 1	471.2-536.5	9.3-79.9	75.7
stage 2	584.0-670.2	11.4-88.5	102.3
FAX stage 1	525.0-589.0	4.8-68.5	126.1
FBM stage 1	587.2-691.6	9.9-95.7	98.3
FBC stage 1	476.0-568.6	9.7-79.8	58.4
stage 2	634.4-718.1	19.7-95.3	105.4
FAZ stage 1	569.1-633.2	11.1-95.6	148.2
SBP stage 1	666.3-748.1	10.1-90.4	143.7
SDS stage 1	618.6-667.1	9.2-95.1	239.6
SAX stage 1	571.1-614.3	7.0-66.6	194.1
stage 2	703.8-771.8	19.7-95.0	166.8
SBM stage 1	644.3-769.7	9.6-95.7	101.2
SBC stage 1	528.0-603.7	9.0-78.6	87.15
stage 2	700.6-779.4	20.6-95.1	140.1
SAZ stage 1	536.4-579.1	9.6-79.5	161.5
stage 2	624.8-664.5	21.8-80.2	150.1
stage 3	713.2-765.1	22.4-95.9	209.6

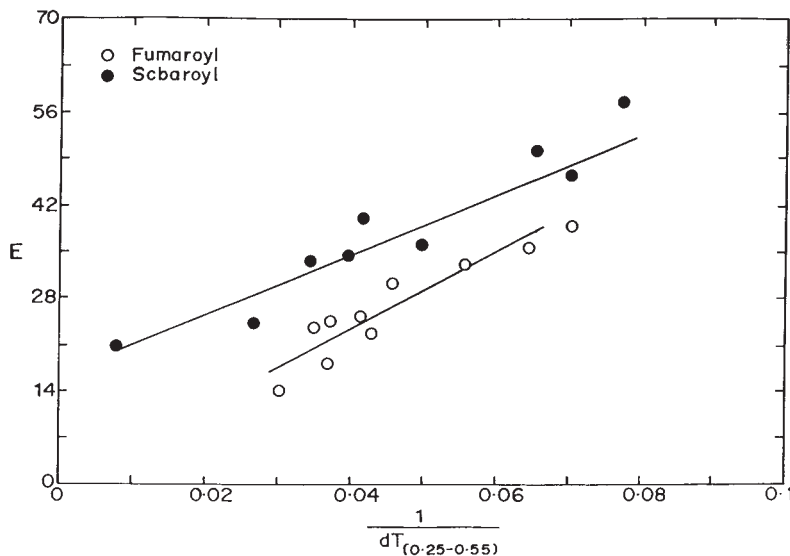


Figure 11 Relationship between energy of activation and apparent degradation rate for two series of polyesters.

may be explained by the stable azomethane linkage formed at higher temperature.

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