

Study on Degradation Reactions in Polyethylene Terephthalate Containing 5-sulpho Isophthalyl Moieties

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ABSTRACT: Kinetics of thermal degradation occurring on polyester containing cationic dyeable comonomer units *viz.* 5-sulphoisophthalate moieties are studied by measurement of changes in intrinsic viscosity and carboxyl values on the polymer after subjecting the polymer chips to temperatures in the range 275–285°C for different residence times ranging from 5 to 60 min and comparing with the homopolymer. The activation energy values for degradation are estimated from the kinetic data. Mechanical properties of the textured yarns produced from the partially oriented yarns (POY) spun under different residence times are measured. Yarn produced with higher residence time

has poor mechanical properties. The SEM images of the POY show presence of particles at the surface of the yarn due to polymer degradation. The size of the particles as seen on the surface increase with increase of retention time. Addition of thermal stabilizer helps in controlling the thermal degradation. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2791–2800, 2010

Key words: cationic dyeable polyester; 5-sulphoisophthalate; polymer degradation; textured yarn; mechanical properties; kinetics; mechanism; intrinsic viscosity; SEM analysis; EDX analysis

INTRODUCTION

Polyethylene terephthalate (PET) is one of the most widely used thermoplastic polymers, which is finding a leading position in applications as diverse as fibers, films, and molded products. Its structure is shown in Figure 1.

Amongst the principal products made from PET commodity fibers have traditionally provided the largest outlet for this polymer and they still do so.^{1–5} This is due to its unique physical properties such as strength, drape, abrasion resistance and crease recovery.

Nonionic disperse dyes are used for dyeing of polyester fibers. These dyes diffuse into the fiber and become physically entrapped in the tangle of polymer chains in the amorphous regions. The dye molecules exhibit easy mobility under favorable conditions. Disperse dyes can migrate to the surface and sublime at elevated temperatures resulting soiling of printed grounds, poor rubbing fastness, and other fastness properties. Also, it is not possible to have bright and lively colors in polyester fibers, due to nature of disperse dyes. Bright colors obtained with cationic dyes are possible only in suitably modified polyester.^{6,7}

To make the polyester ionically dyeable, ionic comonomer species, such as sodium salt of 5-sulphoisophthalic acid, are incorporated into the polymer backbone. The structure of cationic dyeable polyester containing 5-sulphoisophthalate comonomer units (SIPM) is shown in Figure 2.

The anionic sulphonate groups allows the attachment of cationic dye molecules, resulting in brilliant colors and deep shades on fabrics.^{6–8} Incorporation of the comonomer results in copolymer thereby enhancing the rate of dyeing too.

The copolymer structure breaks up the regularity of repeating ethylene terephthalate units of PET thereby inhibiting the formation of crystalline regions during fiber manufacture. These copolymers are known to be hydrolytically less stable compared with the homopolymer—polyethylene terephthalate.^{9,10} The presence of isophthalate comonomer units also promote thermal degradation through increased chain flexibility and more favorable bond angles in the polymer chain.

In this paper, the kinetic studies of thermal degradation occurring in PET having cationic dyeable comonomer units *viz.* 5-sulphoisophthalate moieties are presented. Industrially, PET polymer is produced by batch or continuous polymerization method. The polymer melt is then extruded in a process called melt spinning typically done at 285–290°C over 5–60 min. The resulting filaments can either be wound on bobbin as partially oriented yarn (POY) or collected as “spun tow” in the staple fiber process. In the

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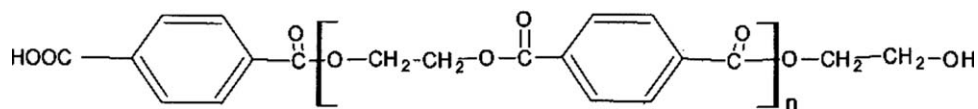


Figure 1 Structure of homopolymer PET.

filament route, the POY is subsequently textured to give the final textured yarn (PTY). In the melt spinning stage, degradation is a common occurrence. These degradation processes are tracked by measuring the mechanical properties of the textured yarns produced from the POY spun at different residence times. The surface properties of the POY spun at different times are also examined by SEM studies.

EXPERIMENTAL

Homo PET fiber grade chips (produced in Batch Poly Reactor at Reliance Industries Limited (RIL), Plant 1, is referred to as Polyester A. Cationic dyeable PET copolymer fiber grade chips produced in the same plant 1 are referred to as Polyester B. Polyester B is also produced with different levels of phosphoric acid as a thermal stabilizer. The properties of the Polyesters A and B are given in Table I.

Determination of the intrinsic viscosity

The intrinsic viscosity (IV) of PET was measured in a solvent mixture of phenol and 1,1,2,2-tetrachloroethane (6 : 4 w/w) at 25°C using an Ubbelohde viscometer by the standard method.

Determination of diethylene glycol content

Polymer sample is refluxed at $\sim 105^\circ\text{C}$ for 30 min with 2-amino ethanol and benzyl alcohol for releasing diethylene glycol (DEG) molecules from the polymer. After separation of the terephthalic acid by filtration of the digested solution, the diethylene glycol (DEG) content is analyzed by GC (GC-FID), by the standard method, using benzyl alcohol as the internal standard.¹¹

Carboxyl groups measurement

Samples of the polymer or fiber (~ 0.5 g) are dissolved in 25 mL of *o*-cresol at 100–110°C and the so-

lution is diluted with chloroform, and the carboxyl terminal groups are determined by titration at room temperature using methanolic KOH (0.02 N) and bromo phenol blue as indicator.

Determination of sodium sulphoisophthalate content in the polymer

The polymer is ashed by heating at 650°C, the ash is dissolved in HCl (1 : 1 w/w), and the sodium content of the solution is determined by AAS. From the sodium content thus found, the amount the sodium sulphoisophthalate content is estimated.

Determination of surface cyclic trimers

Surface cyclic trimer (SCT) is quantitatively determined, after extraction of the fiber with carbon tetrachloride, and measuring of the solution at 287 nm using a Shimadzu Spectrophotometer-UV-1601/make.

Degradation studies

Degradation studies are done on Polyester A and Polyester B. Degradation studies one by heating the chips in Brabender Batch Mixer (rpm 10) under N_2 atmosphere at temperature 270, 275, and 280°C and for residence time 10, 20, 30, 40, 50, and 60 min. Degradation studies for Polyester A were done at temperatures 272, 278, and 285°C and for residence time 5, 10, and 15 min. The samples were analyzed for IV and for increase in COOH end groups. The results are plotted in Figure 5(a,b) for Polyester A and Figure 5(c,d) for Polyester B.

MELT SPINNING OF PET CHIPS INTO POY

Polyester B was melt spun into

POY of 128 denier \times 72 filaments at RIL Plant 1. The yarn is referred to as POY B. The spinning process used the following conditions:

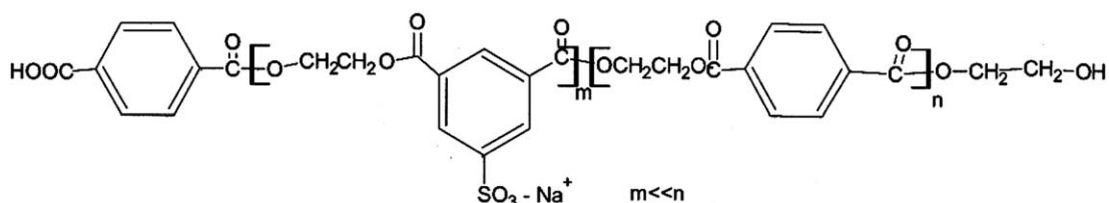


Figure 2 Structure of 5-sodium sulphonate isophthalate copolymer of PET.

TABLE I
Polymer Properties Polyesters A and B

Polyester	Monomer used	IV ^a (dL/g)	Carboxyl end Group (meq/kg)	SIPM ^b content (wt %)	DEG (wt %)	TiO ₂ content (%)	Melting temperature (°C) (DSC)
Polyester A	TPA, EG	0.62 to 0.66	35	—	1.0	0.28	256
Polyester B	TPA, EG, SIPM	0.497 to 0.53	39	2.1	3.1	0.27	246.5

^a IV-intrinsic viscosity.

^b SIPM-5-sulpho isophthalic acid dimethyl ester.

Melt temperature: 280°C, spinning speed: 2735 m min⁻¹

Hold up time (residence time in melt stage): 8 to 65 min.

The yarn Denier, Draw Tension (indirect measure of polymer chain orientation), and tensile properties were measured.

The same yarn was also examined by SEM/EDS to study the effect of processing conditions on yarn surface.

Texturing of POY

The POY is used as a feed stock for texturizing process. Texturizing is done on a Scragg SDS-900 Draw texturing machine with 1-7-1 PU Positorque friction

head twisting assembly at RIL Plant 1. POY yarn was drawn to 1.692 times at the speed of 643 m min⁻¹. Textured yarn properties characterized by Denier, tensile properties, and physical checking of broken filament at taper side of textured yarn packages. Textured yarn produced from POY B is referred to as POY B.

Mechanical properties of the yarn are measured by using Tex Techno Statimat tensile tester.

SEM /EDX measurements of the POY samples are done using FEI quanta 200 ESEM and EDAX system.

RESULTS AND DISCUSSION

¹H-NMR measurement

The Polyester A and B were characterized by ¹H-NMR, recorded on a 300 MHz Varian Mercury 300

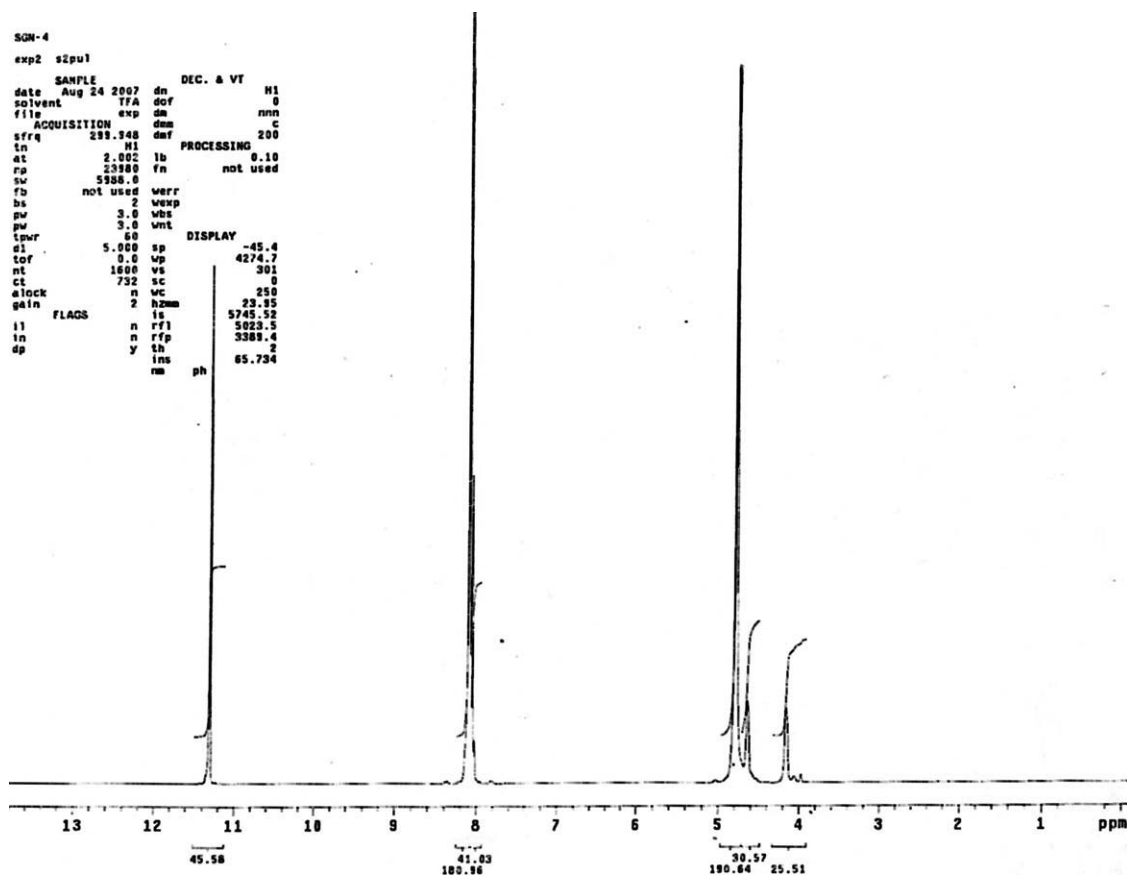


Figure 3 ¹H-NMR spectrum of PET.

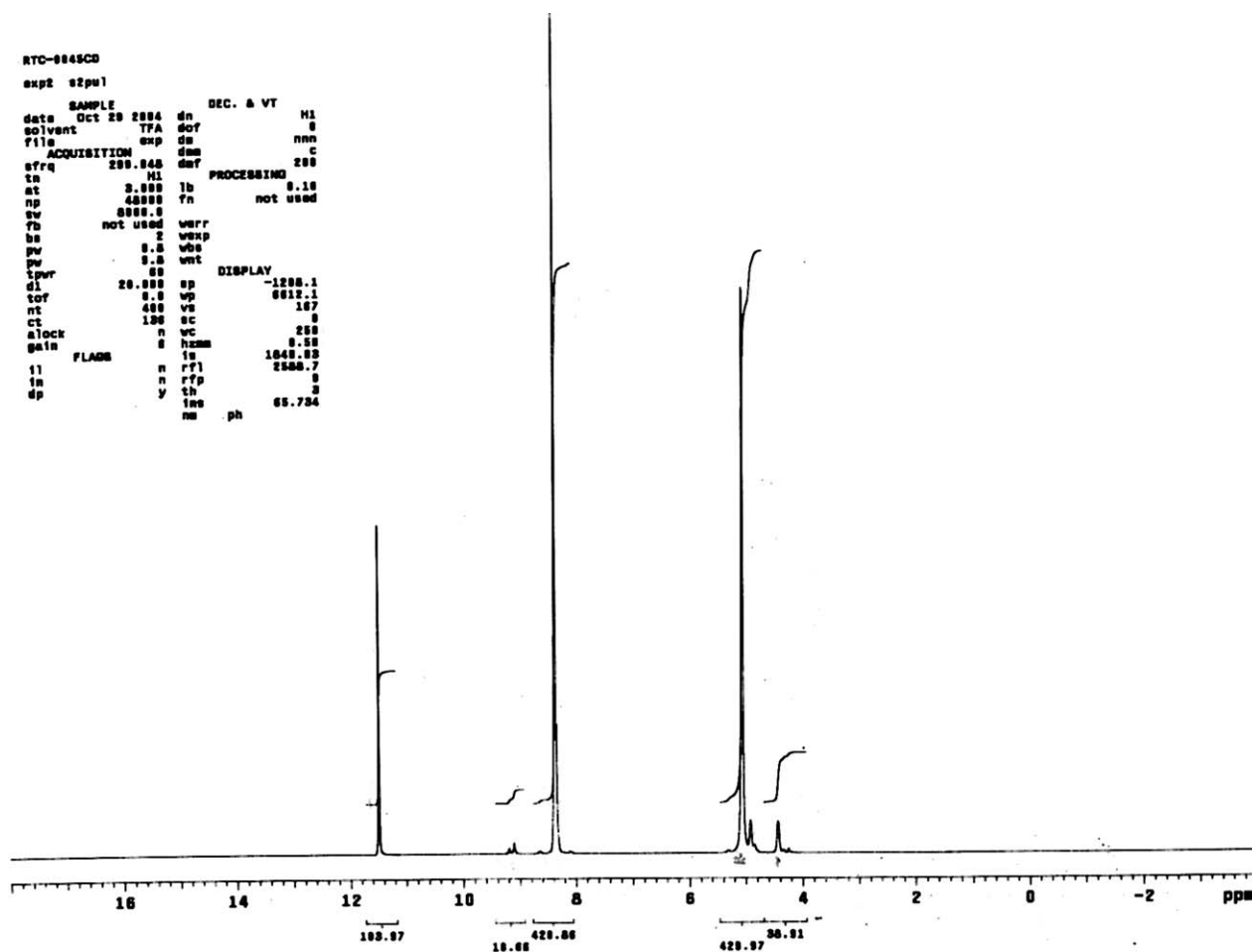


Figure 4 $^1\text{H-NMR}$ spectrum of copolymer.

NMR spectrometer, taken on samples dissolved in TFA-D (deuterated trifluoroacetic acid). The spectra of Polyester A and Polyester B are given in Figures 3 and 4. $^1\text{H-NMR}$ spectra of Polyester A (Fig. 3) show peaks at ~ 4.8 to 5.1 ppm corresponding to the 4 hydrogens of the methylene groups of monoethylene glycol (MEG) units, at 4.16 and 4.64 ppm corresponding to the protons of the DEG units at 4.45 and 4.92 ppm and peaks at 8.0 to 8.1 ppm because of protons of the terephthalic acid units. TFA proton shows a singlet peak at about 11.25 ppm.

Polyester B (Figure 4) shows peaks at ~ 5.0 to 5.1 ppm corresponding to the 4 hydrogens of the methylene groups of MEG units, at 4.42 and 4.92 ppm corresponding to the protons of the DEG units, two peaks at 9.1 and 9.2 ppm due aromatic protons adjacent to sulphonate group of the 5-sulpho isophthalate moiety and an intense peak at 8.3 – 8.4 ppm because of the four aromatic protons of the terephthalate units. TFA proton shows a singlet peak at about 11.5 ppm.

Thus, the NMR spectrum of polymer B confirms that the copolymer has 5-sulpho isophthalyl units incorporated into the backbone.

Polymer properties

The polymer properties shown in Table I indicate that IV of Polyester B is much lower than Polyester A. Sulphonate groups present in Polyester B contributes to ionomer interaction and steric hindrance thereby increasing the melt viscosity. Hence, to ensure good spinnability and reduce breaks, the IV is to be controlled to a lower level, because it can be spun at a relatively low temperature.^{11,12} During the melt polymerization of PET, there occurs an unavoidable side reaction because of coupling of the hydroxyl end groups by dehydration forming DEG units in the chain. The presence of DEG units in the polymer reduces crystallinity, lowers softening point, thermal and hydrolytic stability. About 1 to 1.5 mol % of DEG is always present in PET homopolymer.² Hence, DEG content of the polymer becomes an important parameter to be defined. Table I shows higher DEG content in Polyester B because the sulphonate groups in Polyester B are responsible for catalyzing the DEG generation in the polymer. The melting point of Polyester B is low, when compared with that of Polyester A.

TABLE II
POY Yarn Properties Polyester B (POY B)

S.N.	Residence time (min)	Properties				
		IV (dL /g)	Titre Denier (d)	Draw force (g)	Tenacity (g/d)	Elongation (%)
1	8	0.507	124.1	45.8	2.01	140.9
2	18	–	124.8	44.1	1.98	142.7
3	23	–	124.8	42.6	1.92	143.1
3	40	0.505	125.0	40.1	1.89	145.6
4	65	0.498	125.4	39.0	1.87	147.9

Yarn properties

From Tables II and III, it is seen that in POY, tenacity reduces but elongation increases with higher residence time, whereas for the textured yarn, there is a reduction in tenacity and elongation with higher residence time. This indicates yarn becomes weaker with higher residence time, which is further confirmed by drop in IV of POY and higher broken filament in textured yarn packages. This is also confirmed by estimation of the SCT content, which is more for the yarn produced with higher residence time, as shown in Table IV.

Degradation studies

Figure 5(a,b) gives the variation IV and carboxyl value for the Polyester A when the dry polymer chips are melted and kept at temperatures 272, 278, and 285°C, in inert atmosphere at different times. The data for Polyester B at 270, 275, and 280°C are given in Figure 5(c,d).

Rate of degradation of polymer melts is generally represented¹³ by eq. (1)

$$1/N = 1/N_0 + k_0 E^{-E/RT} t \quad (1)$$

where, N and N_0 are the final and initial number average degree of polymerization, respectively. Where, k_0 is a constant, E is activation energy, R is the universal gas constant, T is temperature in Kelvin, and t is time in minutes.

The degree of polymerization is not an easily measured variable. More commonly, polymer prop-

erties are measured in terms of intrinsic viscosity, and the degradation equation will have to be written using this variable.

The intrinsic viscosity, η can be related to degree of polymerization by the Mark Hownik equation given by eq. (2).

$$\eta = bN^\beta \quad (2)$$

where, η is intrinsic viscosity, b and β are constants depending on the type of polymer.

Substituting eq. (2) in eq. (1), the rate of degradation of polymer melts can be written as eq. (3), where η and η_0 are final and initial intrinsic viscosities

$$1/\eta^{(1/\beta)} = 1/\eta_0^{(1/\beta)} + k_0(1/b)^{(1/\beta)} E^{-E/RT} t \quad (3)$$

The data on Figure 5(a–d) activation energies are evaluated as per eq. (3) are found to be 128.94 kJ mole⁻¹ for Polyester A and 59.22 kJ mole⁻¹ for Polyester B.

These values indicate that the copolymer is more prone to thermal degradation, when compared with the homopolymer. Holland and Hay¹⁴ have shown by Thermal analysis-FTIR spectroscopy the average activation energy for the β C–H transfer process (loss of 1960, 1730, and 1255 cm⁻¹ bands in FTIR) was 230 ± 10 kJ mole⁻¹ and 250 ± 10 kJ mole⁻¹ for PET modified by DEG copolymerization and PET modified with both DEG and IPA copolymerization, respectively. They have also shown that the activation energy for the loss of –O–CH₂–CH₂–OH, i.e., ethylene glycol derived end groups (loss of 3440 cm⁻¹ in FTIR) was $\sim 160 \pm 10$ kJ mole⁻¹. Loss of ethylene glycol end groups leads to the formation of

TABLE III
Textured Yarn Properties Polyester B (PTY B)

S.N.	Residence time (min)	Properties			
		Titre (Denier) (d)	Tenacity (g/d)	Elongation (%)	Broken filament (number/kg)
1	8	78.0	3.16	26.1	0.2
2	18	78.3	3.13	25.4	0.5
3	23	78.0	3.06	25.0	0.8
4	40	78.5	3.06	23.6	1.0
5	65	78.6	2.95	20.5	1.3

TABLE IV
Amount of Surface Cyclic Trimer in POY B

S.N.	Residence time (min)	Cyclic trimer (parts per 10 ⁶ parts (ppm))
1	8	195
2	40	221
3	65	366

a carboxyl end groups, which promotes intramolecular backbiting reactions. The favorable angle of 1,3 structure in the isophthalate unit of the 5 sulpho-isophthalate comonomer unit, facilitates easy degradation process. The presence of bulky sulphonato group causes disorders in the fine structure of polyester fiber thereby lowering the hydrolytic and thermal stability.⁹

The depolymerization and thermo-oxidative degradation results in decrease of IV and a rise in the

number of carboxyl end groups as seen in Figure 5(a–d). Similar phenomena are reported for polyester copolymers at higher temperatures.¹⁵ The degradation processes that occur are influenced by the moisture and oxygen present in the system. PET is shown to give dual slopes of initial fast rate and later slow rate of degradation.¹⁶ The initial rate is attributed to hydrolysis of residual water, and the latter slow rate is attributed to the thermal degradation initiated by thermal energy. Rate of degradation of PET polymer is studied by measurement of the evolved acetaldehyde by Khemani.¹⁷ The degradation causes a decrease in molecular weight either through random scission at the ester linkages or through chain ends.

Mechanism of thermal degradation

The thermal degradation mechanism of polyester segments indicates an essential contribution from

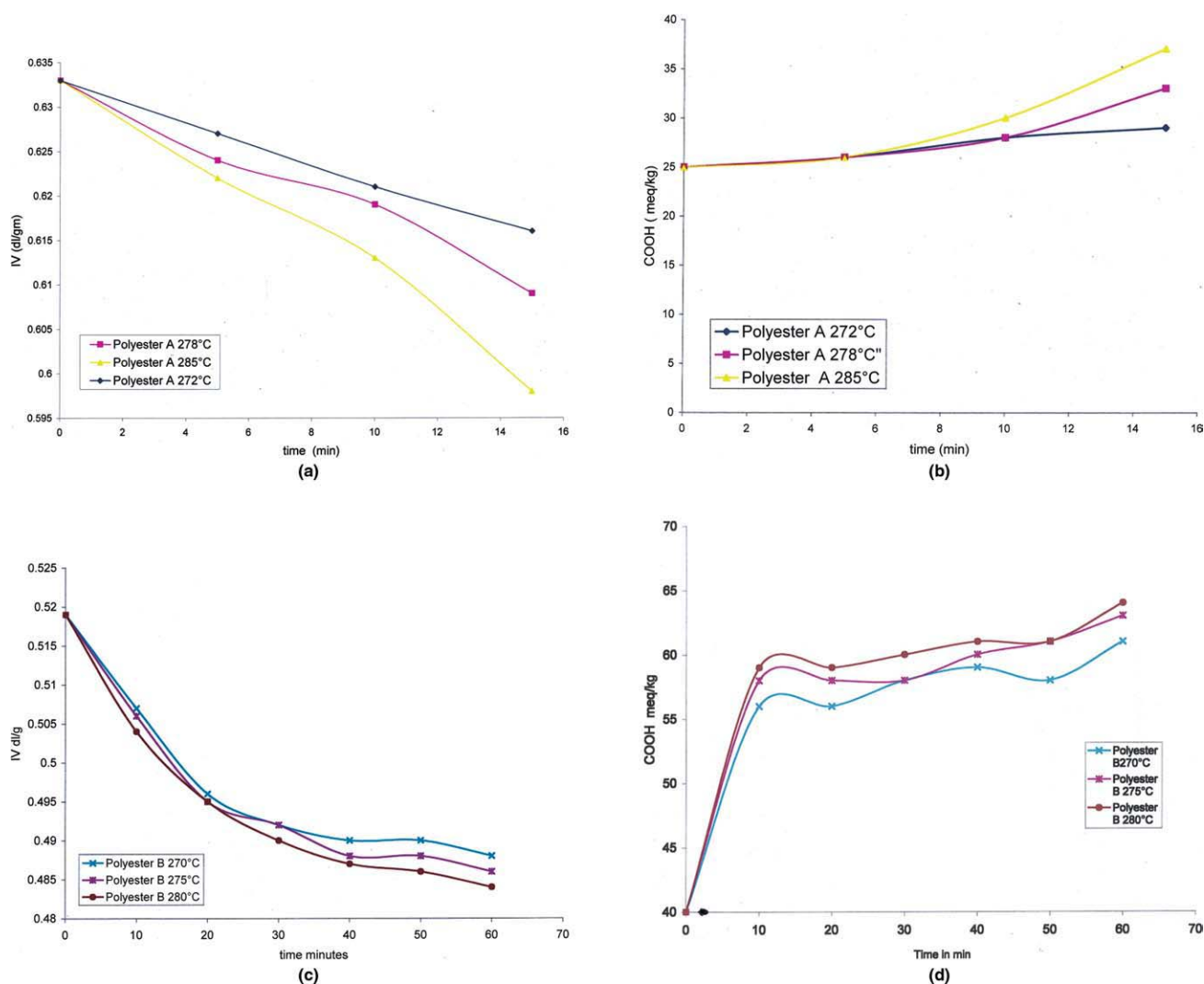
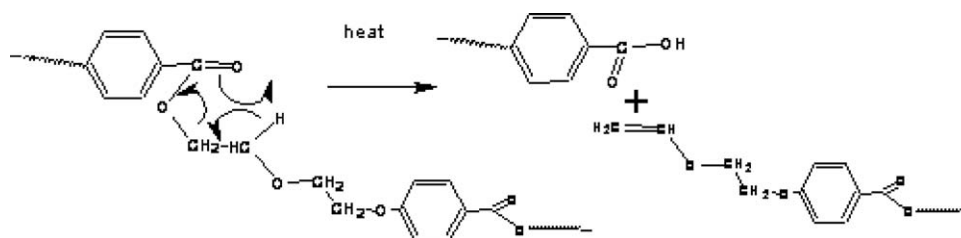
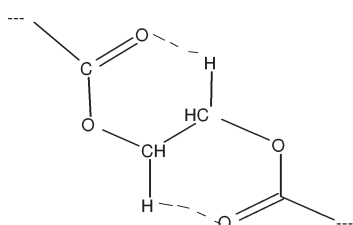


Figure 5 IV data with time of Polyester A, (b) COOH data vs. time for Polyester A, (c) IV data vs. time for Polyester B, and (d) COOH data vs. time for Polyester B. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 1 Mechanism of degradation.

inter or intra molecular hydrogen shifts¹⁸ involving the β hydrogen transfer process in PET moieties taking place as shown, which results in mid chain scission leading to higher acid numbers.



inter or intra molecular hydrogen shifts in PET

When DEG units are more in the polymer, the thermal decompositions proceeds more readily and being favored by the increased acidity of the β hydrogens having no interference from the opposing ester as shown in Scheme 1.¹⁹

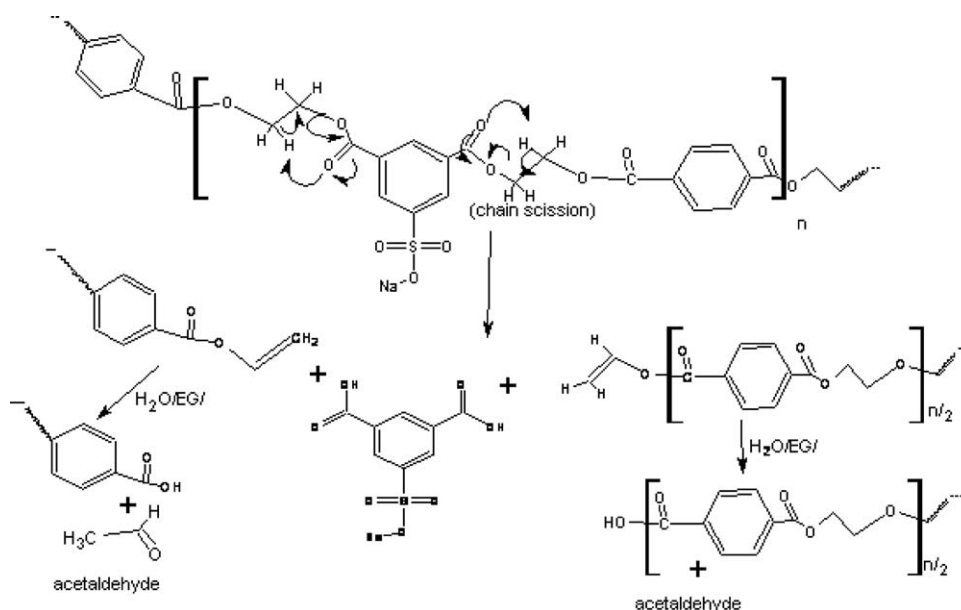
The degradation occurs by three different routes involving the hydroxyl end groups or vinyl end groups or by the inexhaustible mid chain scission route.^{16,18,19} Based on the mechanism of end group

scission of hydroxyl and or vinyl end groups and that of mid chain occurring simultaneously during thermal degradation, the by-product formed has two carboxyl terminals, indicating higher acid value in the resulting product. The proposed mechanism for degradation is given in Scheme 2.

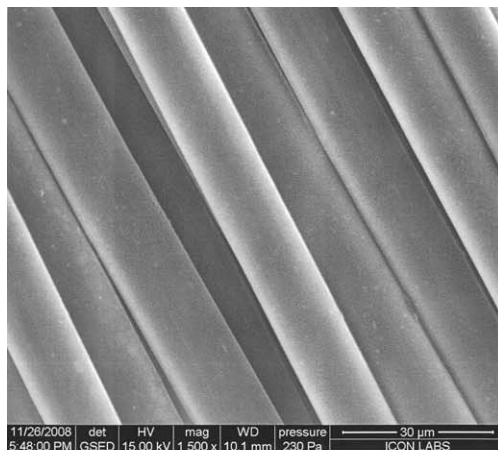
SEM/EDX measurements

The SEM pictures taken for POY B, made with a residence time 8, 40, and 65 min are given in Figure 6(a), 6(b), and 6(c), respectively. Surface of the POY B produced with higher residence time [Fig. 6(b,c)] is found to be very rough, whereas the surface of POY B produced with lower residence time is found to be smooth [Fig. 6(a)].

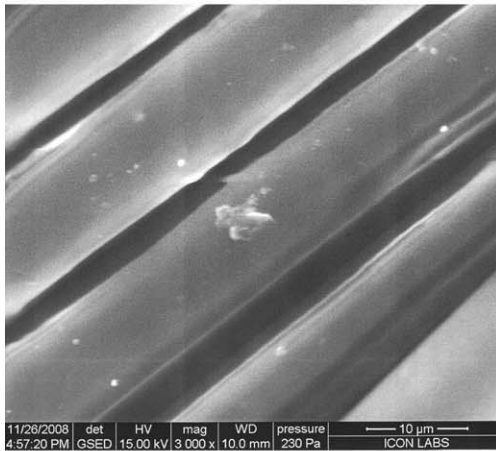
Figure 6(a) shows particles of <1 micron on the surface of yarn, whereas Figure 6(b,c) show formation of particles/lumps of the order of 4–5 microns on the surface of yarn. The degradation products are the highly crystalline cyclic trimers or linear oligomers. The latter have carboxyl terminals on both



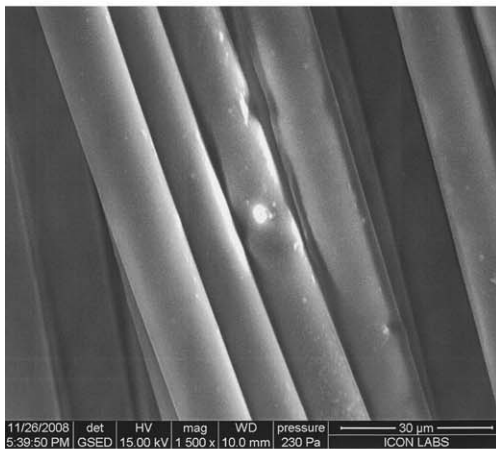
Scheme 2 Mechanism of degradation.



(a)



(b)



(c)

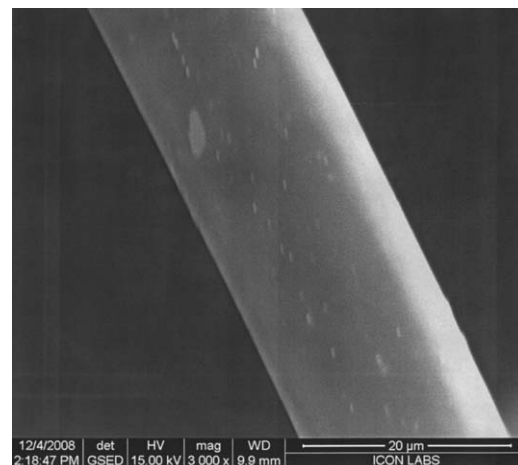
Figure 6 (a) X1500 and X6000 SEM pictures of POY B (residence time, 8 min), (b) X3000 and X3000 SEM pictures of POY B (residence time, 40 min), and (c) X1500 and X6000 SEM pictures of POY B (residence time 65 min).

sides which form crystals with sharp edges and are not soluble in the molten mass and hence tend to ooze out to the surface. The SEM images indicate presence of larger particles in the samples, which

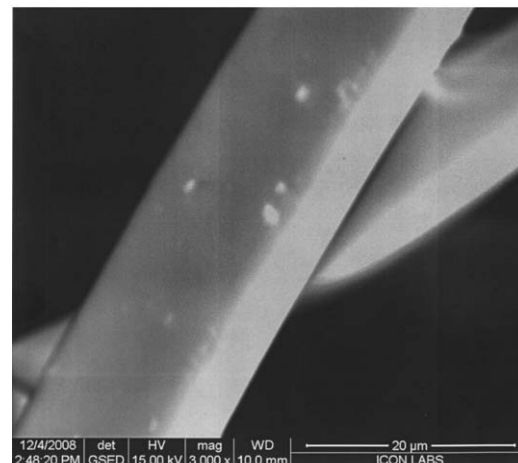
were subjected to higher residence time in the molten state. This is because when the polymer is kept in the molten state for longer period of time, the degraded products tend to grow in their size [Fig. 6(b,c)], with sharp edges which create weak centers that give rise to broken filament during texturizing.

The EDX analysis of these particles indicate presence of more organic material (i.e., low-molecular weight oligomers of larger particle size) along with some external metallic impurities like Si, Fe, Ti, etc. The particles as seen by EDX are organic and are due to more crystalline species. This is separately confirmed by measuring the surface cyclic trimers (shown in Table IV) in the yarn samples produced with different residence times.

When the yarn was washed with methanol, some of the particles gets washed off as seen by the SEM of the washed material in Figure 7(a,b) indicating the oligomers and cyclic trimers get washed off, with methanol. This confirms that the particles seen in the surface are due to surface cyclic trimers.



(a)



(b)

Figure 7 (a,b) SEM picture of POY B (residence time 65 min) after washing with methanol.

TABLE V
Effect of Phosphoric Acid on the Mechanical Properties of the PTY B

Quantity of phosphoric acid added (parts per 10 ⁶ g)(ppm)	Tensile strength (g/d)	Elongation (%)
0	2.61	12.6
50	2.84	19.6
110	2.89	20.6
125	2.90	22.1
150	3.0	23.7

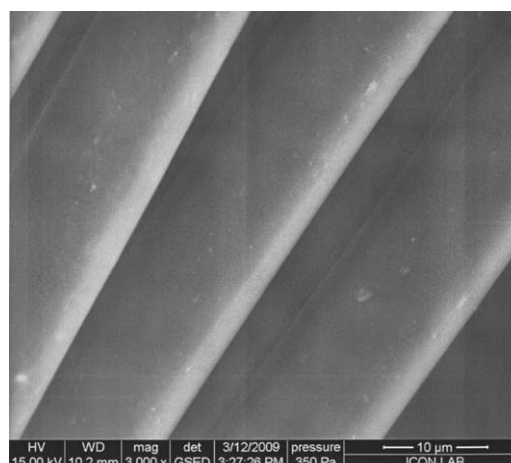
Effect of thermal stabilizer on the thermal degradation

Phosphoric acid is added as thermal stabilizer to reduce the extent of degradation. It is reported that phosphoric acid interact with the polycondensation catalysts thereby modifying the catalyst.²⁰⁻²³ Because the same catalyst catalyzes the thermal degradation addition of phosphoric acid mitigates degradation reactions. The mechanical properties of the textured yarn (PTY B) produced with different amounts of phosphoric acid is given Table V.

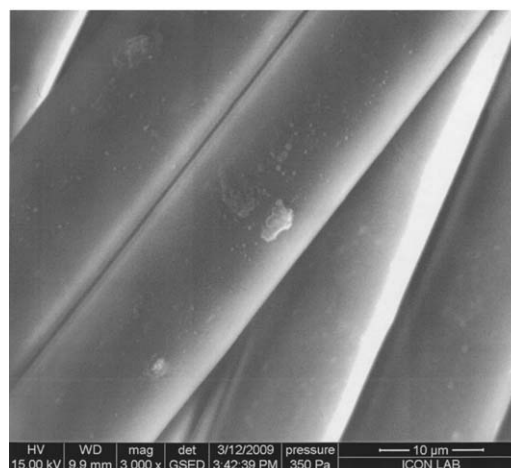
The data in Table V indicate that addition of phosphoric acid improves the mechanical properties of the yarn. But caution is needed on the amount of phosphoric acid used. Figure 8(a,b) shows the SEM pictures of the POY B prepared with different concentration of phosphoric acid in the polymer. The pictures indicate when phosphoric acid is 125 ppm it causes more agglomerate formation, indicating that higher amounts of phosphoric acid results in more agglomerate formation which get oozed out to surface.

CONCLUSION

Kinetic studies on polyester containing cationic dyeable comonomer units indicate that the copolymer degrades faster than homo PET. The rate of degradation depends on the residence time and temperature to which the molten polymer is subjected to. The activation energy values for degradation estimated from the kinetic data are 128.94 kJ mol⁻¹ for homopolymer PET and 59.22 kJ mol⁻¹ for cationic dyeable copolymer. Yarn produced with higher residence time has poor mechanical properties. The SEM images of the yarn samples indicate that as the residence time in a particular temperature is increased more number of particles of degraded products are formed, and they have tendency to grow in large size. The degradation results in highly crystalline trimers or oligomers having carboxyl terminals. Addition of phosphoric acid is able to control degradation.



(a)



(b)

Figure 8 (a) SEM of POY B with 110 ppm H₃PO₄ and (b) SEM of POY B with 125 ppm H₃PO₄.

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