

Structure-Property Relationship in Copolyesters.

I. Preparation and Characterization of Ethylene Terephthalate-Hexamethylene Terephthalate Copolymers*

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Synopsis

Poly(ethylene terephthalate)-containing ethylene and hexamethylene residues in the polymer backbone were prepared by melt condensation reaction of dimethyl terephthalate (DMT) and different quantities of ethylene glycol (EG) and 1,6-hexane diol (H) in the initial monomer feed. Several polyester samples were prepared by varying the mol % of 1,6-hexane diol with respect to ethylene glycol in the initial monomer feed. These included 0.0 (PET), 2.5 (H₁), 5.0 (H₂), 7.5 (H₃), 10.0 (H₄), 12.5 (H₅), 15.0 (H₆), 17.5 (H₇), 20.0 (H₈), 50.0 (H₉), 80.0 (H₁₀), and 100.0 (H₁₁), respectively. The polymers were characterized by recording IR spectra and intrinsic viscosity measurements. The relative thermal stability of the polymers was evaluated by dynamic thermogravimetry in air. An increase in mol % of 1,6-hexane diol resulted in a decrease in melting points and thermal stability of copolymers. PET and copolyesters were spun to fibers by using the melt-spinning technique. The fibers were drawn to draw ratios 2, 3, 4, and 5. In case of copolymers, tensile strength decreases slightly with increasing mol % of H whereas % elongation increases. The moisture regain and dye uptake in copolyesters was greatly enhanced as compared to PET.

INTRODUCTION

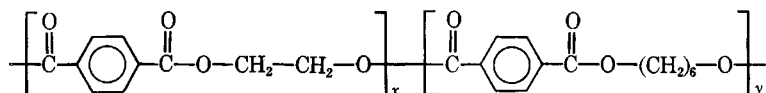
Structural modification of poly(ethylene terephthalate) by varying the glycol or acid content has been investigated in the past with an aim to extend the use of such copolymers in new application areas. The crystallization propensity in polyesters depends to a great extent on the carbon content of the glycol. For example, poly(butylene terephthalate) (PBT) crystallizes at a faster rate than poly(ethylene terephthalate) (PET). The former can crystallize even when quenched from the melt whereas PET can be easily quenched to yield amorphous transparent film.¹ The crystallization rate of PBT can be reduced by incorporation of tetramethylene sebacate groups in the backbone. Structure-property correlations in such copolyesters have been described²⁻⁵ in the literature.

Poly(hexamethylene terephthalate) has been reported to have melting point of ~146°C and percentage crystallinity of 38.⁶ Melting point, crystallinity, and crystallization rates of PET are expected to change by incorporation of hexamethylene units in the backbone. Therefore, it would be of interest to investigate the structure-property relationship in polymers containing hexamethylene and ethylene groups in the backbone. No systematic studies of such copolyesters

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have been reported in the literature although poly(hexamethylene terephthalate) and its random block copolymers with polyethylene oxide have been investigated.^{7,8} In our previous papers, the preparation and characterization of ethylene terephthalate-poly(ethylene oxide) random block copolymers⁹ and ethylene terephthalate (2G)-hexamethylene terephthalate (6G) copolymers¹⁰ have been reported. Improved dye uptake and moisture regain was observed by incorporation of poly(ethylene oxide) in the backbone.

In the present paper, we report the work carried out on some random copolyesters of ethylene terephthalate and hexamethylene terephthalate. The copolymers have been prepared by the melt condensation reaction of dimethyl terephthalate (DMT), ethylene glycol (EG), and hexanediol (H). Such polyesters are expected to have the following structure:



The value of x and y will depend upon the mole % of ethylene glycol and 1,6-hexanediol in the initial monomer feed.

The polymers were characterized by IR spectra, end group analysis, and viscosity measurements. The effect of copolymer composition on thermal stability, melting points, and mechanical properties of fibers was also investigated.

EXPERIMENTAL

Copolymers were prepared by using dimethyl terephthalate (DMT) and different molar ratios of ethylene glycol and 1,6-hexanediol. The details of reaction conditions have been reported elsewhere.¹⁰ An Ubbelohde suspension-level viscometer was used for the determination of intrinsic viscosity at 30°C in *m*-cresol or in phenol-tetrachloroethane (3:5 v/v). Carboxyl end groups in the polymers were determined by acidimetric titration.¹¹

The infrared spectra of polymer films were obtained by using a Unicam SP-1200 IR Spectrophotometer.

A Gallenkamp melting point apparatus was used for determination of melting points. The thermal stability of the polymers was evaluated by dynamic thermogravimetry in air using Stanton TG-750 Thermal Analyzer. A heating rate of 10°C/min and 5 ± 0.1 mg of the polymer sample was used in each experiment.

Spinning of the Polymers to Fibers

The spinning of various copolyesters into fibers was carried out by melt spinning using a bench scale spinning unit. First a candle was prepared from polymer chips from which fibers were spun in the second step.

The spinning conditions were changed according to the melting point and thermal behavior of the polymers. The spinning temperature was kept 10–15°C higher than the melting point of the particular polymer.

The fibers were drawn to different draw ratios using a bench scale drawing machine. As-spun fibers from each polymer sample were drawn to draw ratios (DR) 2, 3, 4 and 5. Drawing temperature was fixed by taking into consideration

TABLE I
Preparation of Polyesters: Conditions of Condensation Polymerization

Sample no.	Sample	Quantities of reagents (mol)			Mol % of H on basis of EG	Temp. of polycondensation (°C)
		DMT	EG	H		
1	PET	0.1	0.200	—	0.0	285 ± 2
2	H ₁	0.1	0.195	0.005	2.5	284 ± 2
3	H ₂	0.1	0.190	0.010	5.0	282 ± 2
4	H ₃	0.1	0.185	0.015	7.5	280 ± 2
5	H ₄	0.1	0.180	0.020	10.0	278 ± 2
6	H ₅	0.1	0.175	0.025	12.5	276 ± 2
7	H ₆	0.1	0.170	0.030	15.0	274 ± 2
8	H ₇	0.1	0.165	0.035	17.5	272 ± 2
9	H ₈	0.1	0.160	0.040	20.0	270 ± 2
10	H ₉	0.1	0.10	0.100	50.0	265 ± 2
11	H ₁₀	0.1	0.04	0.160	80.0	260 ± 2
12	H ₁₁	0.1	—	0.200	100.0	260 ± 2

the crystallization temperature of each polymer sample from DTA measurements.

Heat setting of the fibers drawn to DR:5 was carried out in an air oven at 135°C for 30 min. The fibers were wound loosely on a metallic zig allowing 2% shrinkage.

The denier of the fibers was determined by weighing 10 m of fibers on a sensitive balance. From this the weight of 9000 m of fibers was calculated.

The mechanical properties of the fibers were evaluated by an Instron tensile tester under standard condition. A full scale load of 100 g, crosshead speed of 5 cm/min, gauge length of 4 or 3 cm, and chart speed of 5 cm/min were used.

The moisture regain of the fibers was determined by vacuum desiccator method, using P₂O₅ as a desiccant.

TABLE II
Characterization of Copolyesters

Sample no.	Sample	mp (°C)	Intrinsic viscosity [η] (cm ³ ·g ⁻¹) in			K' ^a	Carboxyl equivalent wt
			<i>m</i> -Cresol		Phenol + tetrachloroethane at 30°C		
			At 35°C	At 30°C			
1	PET	260	—	49.6	64.0	0.406	10500
2	H ₁	256	33.0	40.0	65.0	0.267	9750
3	H ₂	242	37.0	47.0	62.0	0.307	8875
4	H ₃	232	32.0	39.0	61.0	0.335	9250
5	H ₄	224	31.0	32.0	60.5	0.412	8750
6	H ₅	214	47.0	—	58.0	0.309	8000
7	H ₆	206	35.0	—	64.0	0.435	6750
8	H ₇	200	45.5	—	68.0	0.432	8250
9	H ₈	188	46.0	—	70.0	0.346	7250
10	H ₉	128	16.0	21.0	43.0	0.196	3868
11	H ₁₀	146	19.0	24.0	45.5	0.227	5475
12	H ₁₁	151	24.5	27.5	49.0	0.138	5832

^a K' values were obtained in the phenol + tetrachloroethane mixture.

The dyeing of the fibers was done with a disperse dye (Cibacet Red 2G-C.I. Disperse Red-17) in a beaker dyeing machine at 110°C and at pressure of 5–7 lb/in.² without using a carrier. For each experiment, 50 mg of fibers was used. Dyeing was done for 1.5 h at boil. At the end, the samples were taken out, rinsed with a water–acetone mixture (70:30), and then dried at room temperature.

The dye uptake was estimated by dissolving 5 mg of the dyed fiber samples in 10 mL of *o*-chlorophenol. The optical density was measured by using a Unicam SP-600 Spectrophotometer at the wavelength of maximum absorption. The dye uptake of each sample was calculated (mg dye/100 mg fiber).

For testing the lightfastness, a parallel bunch of fibers of each dyed sample was pasted on a thick white paper with the help of cellophane tapes. The paper was mounted on a frame, and samples were exposed with MBTF Phillips 500-W mercury lamp. The exposure was continued for 72 h, and the dye fading was visually compared with the unexposed samples.

RESULTS AND DISCUSSION

In Table I, detailed conditions of condensation polymerization are given. The intrinsic viscosity of the polymers was determined at 30°C and 35°C in *m*-cresol (Table II).

The intrinsic viscosity of polymers was lower in *m*-cresol at 35°C than at 30°C. The effect of temperature on intrinsic viscosity can be explained in terms of two opposing factors: (a) thermal motion which increases with the temperature and decreases the viscosity and (b) increase in solvent power with increase in temperature which will tend to increase the viscosity. The effect of solvents on intrinsic viscosity was studied by determining $[\eta]$ in phenol–tetrachloroethane mixture at 30°C. The observed values of $[\eta]$ were higher in the phenol–tetra-

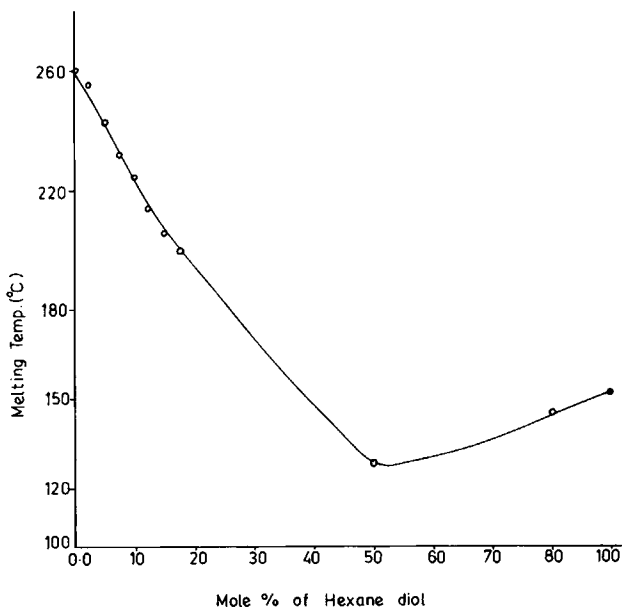


Fig. 1. Melting point vs. composition plots for poly(ethylene terephthalate) copolyesters.

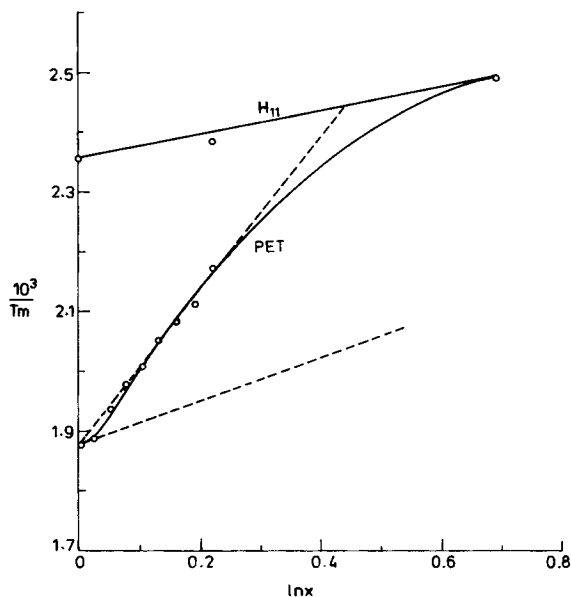


Fig. 2. Plot of $1/T_m$ vs. $\ln X$ for poly(ethylene terephthalate) copolyesters.

chloroethane system than in *m*-cresol which may be due to difference in the hydrodynamic volume of the polymer in the various solvents. If a solvent interacts poorly with polymer, polymer-polymer contacts are more probable, and therefore the chain coils up. If the solvent interacts well with the polymer, polymer-solvent contact will be more probable than polymer-polymer contacts, and the chain will expand. The coiled chain offers less thermodynamic resistance than an uncoiled one, and therefore the viscosity of polymer solution in relatively poor solvents would be lower than in good solvent. The value of Huggins constant K' (Table II) lies in the range 0.3–0.4 in most of these polymers except in H_9 , H_{10} , and H_{11} samples in which low value of K' was observed.

Carboxyl equivalent number was determined by titration (Table II) with alkali. An increase in hexamethylene units in the backbone resulted in a decrease in this value, suggesting lower molecular weights of copolyesters. The melting point of copolyesters decreased with increasing mol % of 1,6-hexane diol in the initial monomer feed (Table II). The lowest mp was observed in H_9 copolyester sample. A decrease in the melting point of PET containing adipic acid or sebacic acid as third component has been reported earlier.^{3,12} A lower melting point of H_{11} , i.e., poly(hexamethylene terephthalate), than PET has been reported in the literature. The difference in the melting points of PET and hexamethylene terephthalate polymers illustrates the effect of increasing flexibility between the ester groups. The consequent decrease was observed in mp on the incorporation of different mol % of the 1,6-hexane diol in the polyester backbone.

The melting point composition diagram of copolyesters is shown in Figure 1. The main feature of the curve is an eutectic point observed when 50% of ethylene groups in PET were replaced by hexamethylene groups.

Using the theory of melting points of copolymers, the heat of fusion (ΔH_f) of PET and H_{11} can be calculated from the copolymer melting points (T_m) by

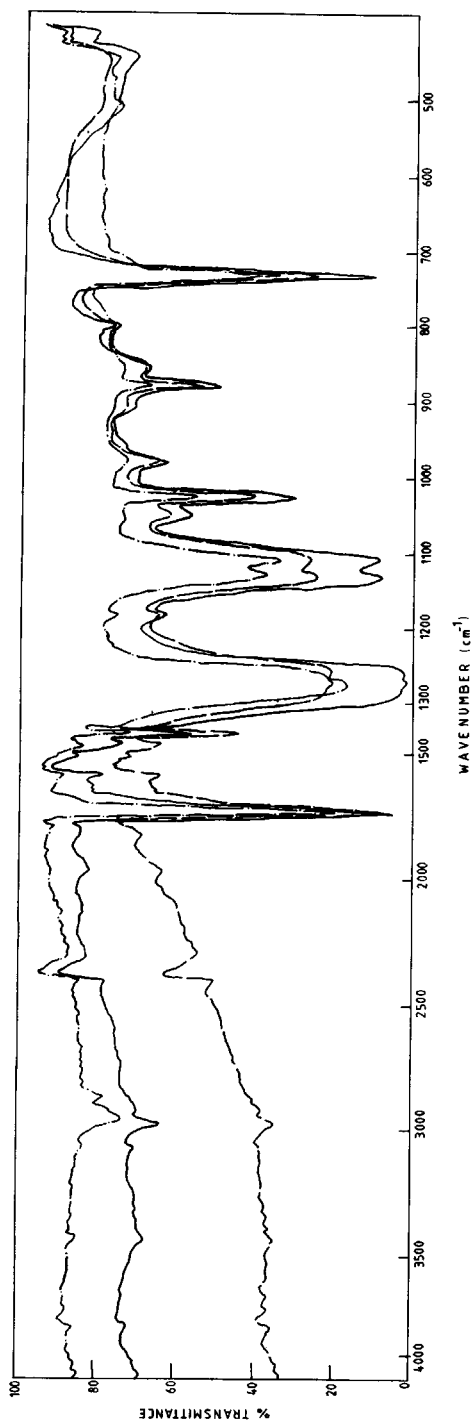


Fig. 3. IR spectra of polyesters: (—) PET; (---) H₁; (-·-·) H₈.

TABLE III
 Characteristic IR Band Position in Polyester and Copolyesters (cm⁻¹)

PET	H ₁	H ₈	H ₁₁	Assignment
730	730	730	728	C—H bending
798	798	798	798	Phenyl C—C in plane
850	850	850	—	Trans and gauche conformation of glycol segments
—	—	—	840	
876	876	876	876	C—H phenyl bending
978	978	978	968	C—C stretch of glycol segments
1025	1025	1025	1020	C—C stretch of glycol segments
1045	1045	1045	—	
1110	1110	1110	1100	—C—O—C— stretching
1130	1130	1130	1110	—C—O—C— stretching
1180	1180	1180	1175	—C—O—C— stretching
1280	1260–1285	1260–1285	1240–1290	—C—O—C— stretching
1358	1358	1358	1358	—CH ₂ — wagging
1420	1420	1420	1420	Phenyl —C—C— (in plane)
1465	1465	1470	1490	—CH ₂ — wagging
1510	1510	1510	1515	Phenyl—C—C— (in plane)
1595	1595	1595	1595	Aromatic C=C— stretching
1740	1740	1740	1725	—C=O stretching
2970	2980	2960	2970	—C—H stretching

Flory's equation:

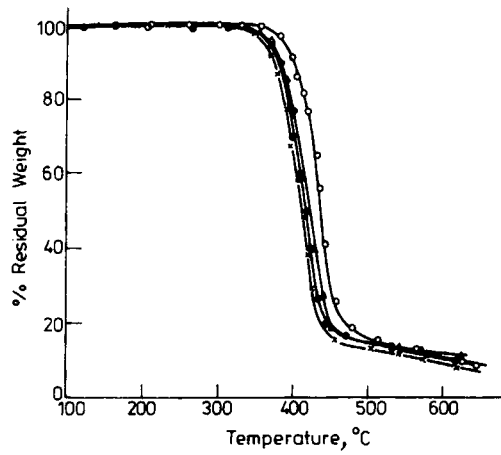
$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_f} \ln X$$

where T_m^0 = melting point of the poly(ethylene terephthalate), T_m = melting point of the copolymers, and X = mole fraction of the ethylene terephthalate in the copolymer. From the slope of $(1/T_m)$ vs. $\ln X$ plot (Fig. 2), $R/\Delta H_f$ values were calculated. Heat of fusion (ΔH_f) was 5500 cal/mol for PET and 8425 cal/mol for H₁₁ as calculated from the initial slope of the curves. These values are of the same order as reported in the literature.¹³ However, if the steep portion of the curve is taken, then the heat of fusion per ethylene terephthalate unit was found to be 1463 calories/mol.

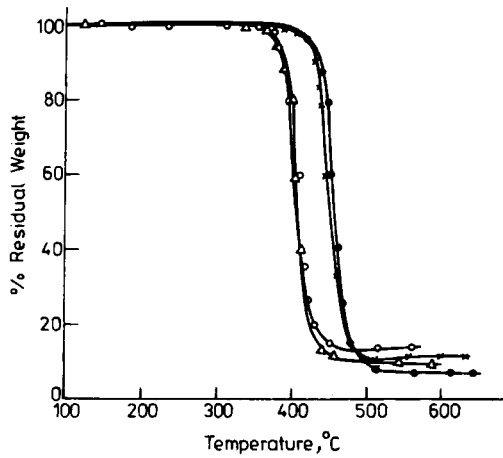
Ishibashi¹⁴ has reported the mp vs. composition relationship in polyether-ester copolymer system prepared from methyl *p*- γ -hydroxypropoxy benzoate and bis- β -hydroxyethyl terephthalate which showed a eutectic type of behavior. Izard¹⁵ has earlier discussed the effect of composition on selected physical properties of several linear polymers including ethylene terephthalate (2gT) and ethylene sebacate (2g10) copolymers. The melting points of these copolymers go through a minimum at 40:60 ratio of 2gT and 2g10.

In the IR spectra of these polymers, absorption bands characteristic of polyesters were present (Fig. 3). The prominent absorption bands along with their assignments have been summarized in Table III. The spectra of PET and various copolymers were similar, only in H₁₁ an extra peak was observed at 840 cm⁻¹.

Thermogravimetric traces obtained by heating the samples in air atmosphere at a heating rate of 10°C/min are shown in Figures 4(a) and 4(b). From these plots the initial decomposition temperature (IDT), integral procedural decom-



(a)



(b)

Fig. 4. (a) Thermogravimetric traces of copolyesters in air atmosphere: (O) H₁; (Δ) H₂; (●) H₃; (X) H₄. (b) Thermogravimetric traces of copolyesters in air atmosphere: (O) H₅; (Δ) H₆; (●) H₇; (X) H₈ (scale has been shifted along *x*-axis for samples H₇ and H₈ by 50°C).

TABLE IV
Thermal Behavior of Copolyesters

Sample no.	Sample	IDT (°C)	IPDT (°C)	<i>T_f</i> (°C)
1	PET	319	471.0	435
2	H ₁	360	432.5	455
3	H ₂	345	425.0	458
4	H ₃	338	420.0	440
5	H ₄	331	417.5	440
6	H ₅	365	410.0	425
7	H ₆	363	407.5	425
8	H ₇	360	412.5	425
9	H ₈	357	407.5	425
10	H ₉	315	361.5	375
11	H ₁₁	311	346.5	370

TABLE V
Spinning and Drawing Conditions of Copolyesters

Sample no.	Fiber sample	Temp. for candle preparation (°C)	Temp. for spinning (°C)	Drawing temp. (°C)
1	PET	252	270	125
2	H ₁	250	266	120
3	H ₂	230	245	115
4	H ₃	220	240	112
5	H ₄	212	228	105

position temperature (IPDT), and final decomposition temperature (T_f) were noted and the values are given in Table IV. The IDT values of the copolymer were higher than those of PET but were found to decrease with increasing mol % of hexamethylene units in the backbone. In the H₉ and H₁₁ samples a significant decrease in IDT values was observed.

The integral procedural decomposition temperatures (IPDT) were calculated in the temperature range of 100–500°C for all the polymer samples.¹⁶ The IPDT values (Table IV) also indicated that the introduction of flexible units in the backbone reduced the thermal stability.

The initial decomposition temperatures of these polymers were found to be higher than the melting points. Hence the polymer can be spun into fibers by melt-spinning technique at a temperature 10°C higher than the melting points without significant degradation.

The spinning condition of various polymers are given in Table V. From the stress-strain curves of the fibers [Figs. 5(a) and 5(b)] tenacity, percent elongation, and initial modulus were calculated (Table VI). In case of copolyester fibers, a slight decrease in tenacity and an increase in percent elongation was observed with increasing mole percent of hexamethylene units in the backbone. The initial modulus was less as compared to PET and decreases with increasing mole percent of hexamethylene groups.

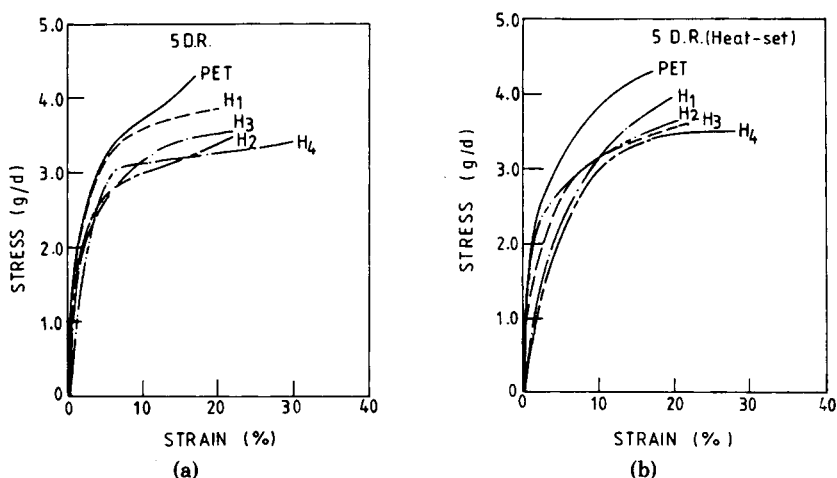


Fig. 5. (a) Stress-strain curves of copolyester fibers (DR:5). (b) Stress-strain curves of heat-set fibers (DR:5).

TABLE VI
Mechanical Properties of Copolyester Fibers

Sample no.	Fiber sample	Draw ratio	Denier	Tenacity (g/den)	Elongation (%)	Initial modulus (g/den)
1	PET	3	16.50	2.2	98	31.2
		4	10.20	3.2	44	51.9
		5	9.14	4.3	17	72.2
		5 ^a	9.14	4.3	17	72.2
2	H ₁	3	12.51	1.96	125	21.0
		4	9.95	2.67	50	21.5
		5	8.20	3.87	20	61.0
		5 ^a	8.20	3.95	20	65.0
3	H ₂	3	21.96	1.20	125	15.0
		4	14.76	2.26	45	19.5
		5	10.42	3.46	22	50.0
		5 ^a	10.42	3.60	20	50.0
4	H ₃	3	11.20	1.60	156.5	6.0
		4	10.11	2.45	68.5	13.0
		5	9.30	3.58	22	46.25
		5 ^a	9.30	3.67	22	48.30
5	H ₄	3	11.32	1.598	175	7.0
		4	9.85	2.40	75	15.0
		5	7.72	3.41	30	43.0
		5 ^a	7.72	3.53	28	45.0

^a Indicates heat-set fibers.

The copolyester fibers show a significant increase in the moisture regain (Table VII) which increased around 25% for addition of 2.5 mol % of hexane diol in the initial feed.

The addition of hexamethylene units modifies the amorphous regions of PET

TABLE VII
Moisture Regain and Dye Uptake of Copolyester Fibers

Sample no.	Fiber samples	Moisture regain (%)	Dye uptake (mg dye/100 mg fiber)
1 PET	As spun	0.51	0.712
	DR:5	0.42	0.216
	DR:5 ^a	0.40	0.182
2 H ₁	As spun	0.66	6.40
	DR:5	0.60	2.88
	DR:5 ^a	0.58	2.80
3 H ₂	As spun	0.74	6.56
	DR:5	0.65	3.60
	DR:5 ^a	0.61	3.60
4 H ₃	As spun	0.78	6.80
	DR:5	0.71	4.16
	DR:5 ^a	0.66	4.06
5 H ₄	As spun	0.82	7.60
	DR:5	0.72	5.04
	DR:5 ^a	0.70	5.00

^a Indicates heat-set fibers.

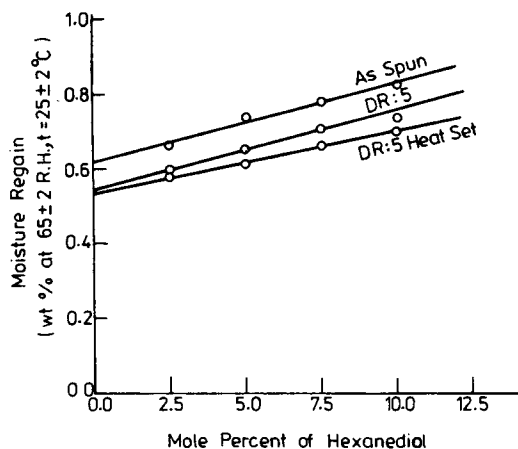


Fig. 6. Moisture regain of copolyester fibers vs. mole % of 1,6-hexanediol in the initial monomer feed.

fibers, which enhances the hydrophilicity of the fibers and may be responsible for higher moisture absorption in the fiber. The as-spun fibers generally have higher values of moisture regain than the corresponding drawn (DR:5) and heat-set fibers. As-spun fibers derived from these polymers are almost amorphous and thus moisture regain is high. Drawing induces crystallization, thus reducing moisture regain. By heatsetting, the crystallization is further increased; hence a marginal decrease in moisture regain value is observed. Figure 6 shows the variation of moisture regain with mol % of hexane diol in fibers of as-spun, DR:5, and heat-set.

Copolyester fibers were dyed to a very deep shade almost 10 times deeper than PET when treated with Cibacet Red 2G using pressure dyeing without carrier. The results of the dye uptake of as-spun, 5 DR and heat-set fibers (DR:5) of various copolyester are given in Table VII. It is obvious from the table that, under all the three conditions, the dye uptake of copolyester fibres was higher than in PET. Pressure dyeing "opens" up the polyester polymer chain, enabling

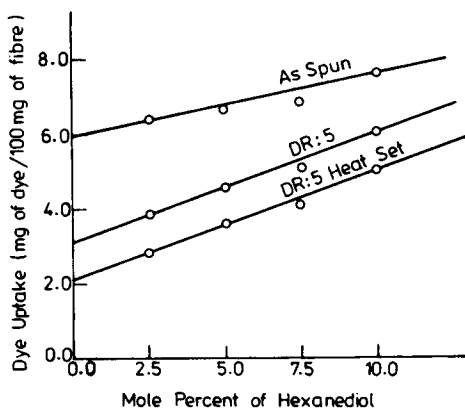


Fig. 7. Dye uptake of copolyester fibers vs. mol % of 1,6-hexane diol (y-axis has been shifted by 1.0 for heat-set fibers (DR:5)).

the dye to penetrate. When the polyester material is removed from the pressure dyeing vessel, the polymer system "closes" again, trapping the disperse dye molecule inside the molecular segments of polymer chain. There is a continuous increase in dye uptake with increasing mol % of hexamethylene units. The increase in dye uptake of copolyester fibers could be accounted for by the increase in moisture content of the fibers which may probably be responsible for more fiber swelling at the dyeing temperature and facilitating the dye penetration in the fibers. It is important to mention that all dyeings were carried out in the absence of carrier. Under these conditions, the commercial PET, as expected, showed very little dye uptake. The dye fading on dyed fibers was found to be of the same extent as that of PET.

On the basis of this work, it may be concluded that moisture regain and dye uptake of PET fibers can be improved by incorporation of hexamethylene groups in the backbone.

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