GRAFT POLYMERIZATION OF ACRYLAMIDE ON POLY (ETHYLENE TEREPHTHALATE) FIBERS AND THE IMPROVEMENT OF ITS SOME PROPERTIES

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SUMMARY

In this study graft-copolymerization reactions of acrylamide with poly(ethylene terephthalate) (PET) fibers were studied by chemical initiation technique using benzoyl peroxide as initiator. We have observed that the extent of grafting depended upon the time, the initiator, and monomer concentration, as well as temperature. The magnitude of the grafting enhanced by increasing benzoyl peroxide concentration up to 4×10^{-3} mole/1 and showed a plateau between 4×10^{-3} mole/1 and 10×10^{-3} mole/1 then decreased by futher increase in benzoyl peroxide concentration. There was also an optimal temperature (75°C) for grafting; below or above this temperature, lower grafting was obtained. On the other hand, the grafting increased upon increase of acrylamide concentration within the range studied. The moisture regain and dyeability properties of the grafted PET were also examined.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers are highly crystalline, markedly hydrophobic, and do not contain chemically reactive groups. Hence, this material is not easily penetrated by dyes of laige molecular dimensions and cannot combine with dye anions or cations. Certain desirable properties (e.g., dyeabilty with acidic and basic dyes; improvement in antistatic properties; therease in moisture regain, etc.) ean be imparted to PET by grafting it with appropriate monomers.

Although PET is one of the most diffucult polymer to be grafted (Memetea 1979), its chemical modification via vinyl graft polymerization has evoked considerable interest during the last decade.

Many useful applications of vinyl monomer polymerization for the chemical modification of PET can be visualized, and many have been reported in the literature (Vlagiu 1973; Faterpeker 1980; Shalaby 1978).

Out of several methods available for grafting the chemical initiation method has been found befitting for the purpose owing to the low degradation of the base polymer. Graft copolymerization onto PET has been accomplished either by high energy radiation using γ-rays from ⁶⁰Co or high energy electrons from accelerators or by chemical means using different initiators such as benzoyl peroxide (Kale 1975; Ohguchi 1982), H_2O_2 (Hebeish 1981).

The aim of the present investigation was to study the graft copolymerization of acrylamide onto PET fibers by chemical methods using benzoyl peroxide, and to investigate the effects of temperature, acrylamide and initiator concentration on the extent of grafting. Variations in the properties such as dyeability and moisture regain of the grafted PET were also evaluated.

EXPERIMENTAL

MATERIALS

Poly(ethylene terephthalate) (PET) fibers (medium oriented, 198 den, 30 flaments) manufactured by SASA (Adana, Turkey) were used after purification by treatment with acetone for 7 h in a Soxhlet apparatus. Benzoyl peroxide (Merck) was twice precipitated from chloroform solution in methanol and was dried in a vacum desiccator for two days (Nozaki 1946). All the compounds (acrylamide, 1,2-dichloroethane, aceton, pyridine e.t.c.) used of chemically pure grade. The acid dye Supracen Red B produced by Bayer was used without further purification.

POLYMERIZATION PROCEDURE

PET was first swollen at 71 °C for 3 h in a solvent/nonsolvent system consisting of 1,2-dichloroethane/water (20/80, $\frac{v}{v}$). Dichloroethane was then removed from the fiber completely by treatment with boiling water. This fiber was then used for subsequent graft copolymerization.

Appropirate concentration of monomer, 5 ml solution of benzoyl peroxide in pure crystylazible benzene and 45 ml water is added on PET (0,3±0.01 g). The mixture was immadiately placed in a thermostated bath adjusted to polymerization temperature. After the desired reaction time the grafted fibers were removed from the polymerization medium and washed several time with water. The sample was then Soxhlet extracted with water for 6 h, dried in an oven at 105°C, cooled to room temperature, and weighed. The increase in weight of the sample divided by its original dry weight and multuplied by 100 will be referred to as percent grafting:

$$\text{Grafting yield (G) \%} = \frac{(\text{dry wt grafted sample})-(\text{dry wt original sample})}{\text{dry wt original sample}} \times 100$$

DETERMINATION OF DYE CONTENT OF DYED SUBSTRATE

The grafted poly(ethylene terephthalate) fiber samples were dyed for 0.5 % shade with acid dyes under the reflux, at 98°C for 1 h, keeping the liquor ratio of 100 at pH 4-4.5. At the end of dyeing the fibers were removed from a dye bath, washed with boiling water for 15 min., soaped in 2 % soap solution at 85°C for 20 min, then again washed with boiling water for 15 min.

For the quantitative determinations the dye was extracted from the fibers with 25 % aqueous pyridine. The eluted dye was determined spectrophotometrically at 528 nm.

DETERMINATION OF MOISTURE REGAIN

The dry samples were conditioned at 65 % relative humidity, at 20°C, and weighed. They were oven dried at 105°C for 3 h, cooled over P_2O_5 in a desiccator and weighed again:

$$\text{Moisture regain \%} = \frac{(\text{wt conditioned sample})-(\text{wt dry sample})}{\text{wt dry sample}} \times 100$$

RESULT AND DISCUSSION

EFFECT OF POLYMERIZATION TEMPERATURE

To investigate the effect of temperature on the extent of grafting, the polymezization reactions were carried out at four different temperatures (70°C, 75°C, 85°C, 92°C).

Figure 1 shows the effect of the polymerization temperature on the extent and rate of grafting of acrylamide onto PET fibres. It is seen that saturation grafting is observed at 75, 85 and 92°C. The effect of raising the polymerization tempeiature up to 75°C is to bring about a significant acceleration in the iate of grafting.
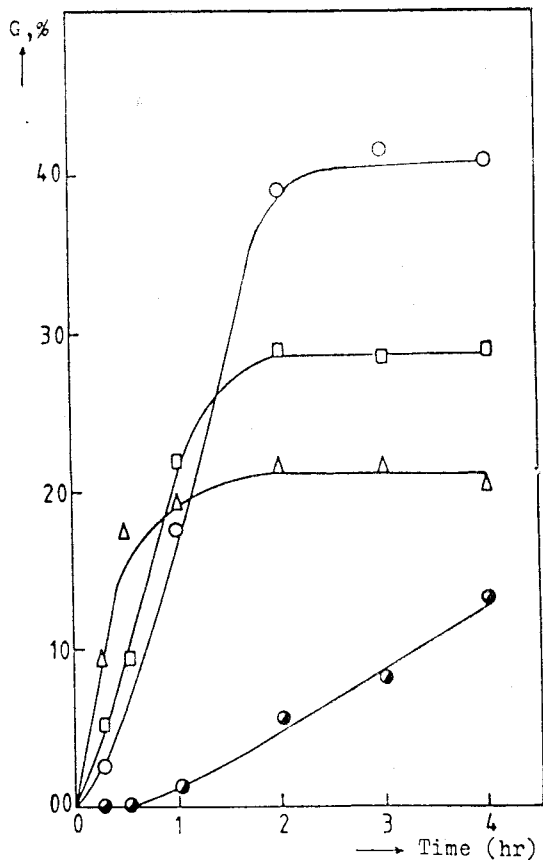

Fig. 1. Effect of temperature on graft yield:
[AAm]; 4 %; [Bz$_2$O$_2$], 4x10^{-3} mole/l; Δ, 92°C; □, 85°C; 0, 75°C; ◐, 70°C.

However, at 70°C the grafting reaction shows an induction period of abouth 60 min, in contiast with grafting at 75, 85 and 92°C where the grafting reaction proceeds without induction periods. At 85°C and 92°C, on the other hand, though the initial iate of grafting is exceedingly higher than that at 75°C yet the saturation grafting

obtained at 85°C and 92°C are much lower than that at 75°C. This situation can be explained as follow: when the polymer passes from the glassy state into a highly viscous liquid the ability to undergo radical reactions becomes increased. Besides this, the favorable effect of temperature on grafting could probably be associated with a faster rate of benzoyl peroxide decomposition, giving rise to more free radicals and higher rate of monomer difussion from the reaction medium to the PET fibers.

It is often observed that rising the polymerization temperature decreases saturation grafting due to the fast rate of termination (Hebeish 1978).

EFFECT OF MONOMER CONCENTRATION

To investigate the effect of acrylamide concentration on the extent of grafting, the polymerization reactions were carried out in the medium having different monomer concentration.

The effect of acrylamide concentration on the graft yield is is shown in Figure 2. It is clear that the increase in the acrylamide concentration from 1.00 to 4.00 g/100 ml is accompanied by a substantial enhancement in the extent and rate of grafting. It must be noted, however, that at low acrylamide concentrations, i.e 1.00 and 2.00 g/100 ml, the graft yield continues to increase with time and no levelling off is attained even after 4 h. Whereas at high acrylamide concentrations, i.e. 3.00 and 4.00 g/100 ml, the grafting reaction proceeds initially at a fast rate, decreases withtime to a slower rate then levels off after about 2 h. Levelling off of grafting could be associated with depletion in monomer and initiator concentration as well as reduction the available sites for grafting on the PET backbone as the reaction proceeds. It seems that the higher amount of graft formation which occured during the initial stages of the reaction acts as a diffusion barrier for reactants.

EFFECT OF INITIATOR CONCENTRATION

Figure 3 shows the effect of benzoyl peroxide concentration on graft yield. It is seen that increasing the benzoyl peroxide concentration up to 4×10^{-3}mole/l is accompanied by a substantial increase in grafting. Although the magnitude of the grafting showed a plateau
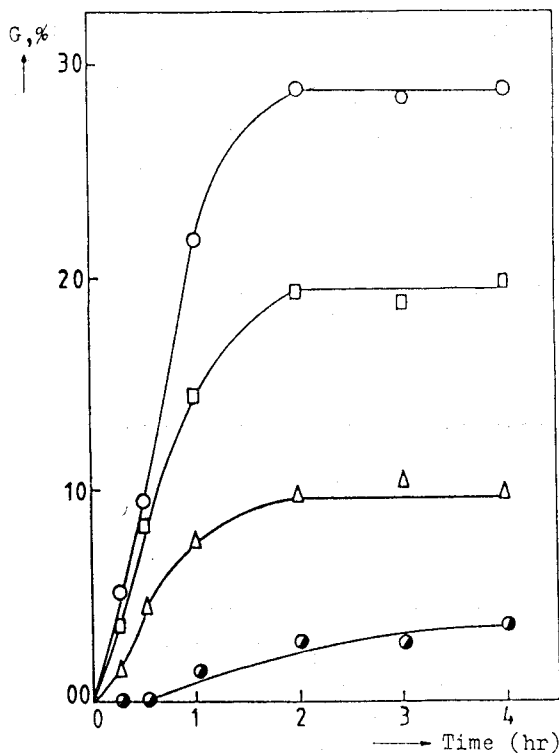
Fig. 2. Effect of monomer concentration on graft yield: temperature, 85°C; [Bz$_2$0$_2$], 4x10^{-3} mole/1,
[AAm] : 0, 4 %; ⬜, 3 %; Δ, 2 %; ◑, 1 %.

between 4x10^{-3}mole/1 and 10x10^{-3}mole/1 of benzoyl peroxide concentration. It can be say that the optimal benzoyl peroxide concentration was 8x10^{-3}mole/1. Further increase in benzoyl peroxide concentration causes a marked fall in grafting.

The free radical and polymeric radical concentration increases with increasing benzoyl peroxide concentration and this consequently leads to an increase in grafting. The further increase in benzoyl peroxide concentration increases the termination reactions (termination with growing polymer chains, and termination with macroradicals of PET) and accelerates the rate of free radical combination. In conclusion grafting yield decreases at high benzoyl peroxide concentration.
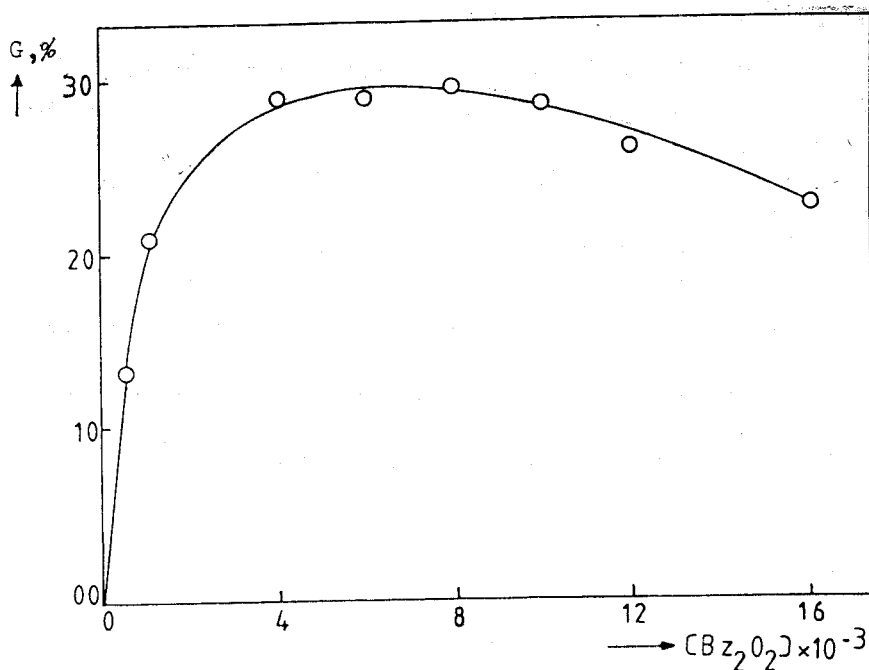
Fig. 3. Effect of initiator concentration on graft yield: temperature, 85°C; reaction time, 2 hr; [AAm], 4 %.

MOISTURE REGAIN AND DYEABILITY

The moistuıe regain of PET fibers grafted with acrylamide increased proportional to the amount of grafting. The moisture regain at 41.71 % acrylamide grafted PET fibers was found to be 3.92 %. Polyester fibers are highly hydrophobic in nature and the moisture content of the fiber is low under normal conditions (0.4 %). Grafting with acrylamide not only brings about the openning of the structure to a certain extent but also increases hydrophilicity of the fiber as a result of the introduction of the polar groups, i.e., an amide group into the fiber matrix. This shift in the hydrophobic nature is responsible for the enhancement of the moisture regain with increasing the percentage of graft yield.

The dyeabliity of fibers grafted with acrylamide increased with acidic dyes. The dyeability of acrylamide grafted PET fibers with acidic dyes related to the $-NH_2$ groups inserted into their structures.

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PREPARATION OF SCHIFF BASE COMPLEXES OF URANIUM (VI), TIN (II) TIN (IV) AND THORIUM (IV) AND DETERMINATION OF THEIR STRUCTURE BY SPECTROPHOTOMETRIC METHODS

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ABSTRACT

$UO_2(II)$, Th (IV) Tın (II) and (IV) complexes with Schiff bases derived from o-nitrobenzaldehyde and p-dimethylaminobenzaldehyde with allylamine have been prepared. The complexes have been characterized by IR spectra and elemental analysis. Magnetic susceptibility of complexes measured. It is concluded that ligand coordinated to metal with allylicnitrogen and coordination number changed according to central atom.

INTRODUCTION

Though, a large number of papers have appeared on metal complexes with Schiff bases derived from aromatic aldehydes and substituted amines, very few ones have been published on Actinide complexes of Schiff bases. The limited information on actinide complexes of Schiff bases prompted us to undertake a systematic search in this field.

In this paper, uranium, thorium and tin complexes of Schiff bases prepared and their structure examined. Schiff bases will be obtained by the condensation of carbonyl compounds, especially aldehyde and ketones, with primary amines. If carbonyl compounds or amins contain effective functional groups, Schiff bases will form effective chelate groups. Chelates can serve as multiple electron-pair donor through several different atoms to a single acceptor atom or ion.

In the present paper Schiff bases derived from p-dimethyl-amino-benzaldehyde and o-nitrobenzaldehyde by the reaction of allylamine in methanol at 25°C. These Schiff bases have been characterized by N.M.R, IR and Mass spectrum. Solid complexes have been characterized by IR and elemental analysis. Magnetic susceptibility measurements have shown that all the complexes are diamagnetic. All the Schiff bases in complexes are coordinated to the metal as monodentate ligand where the allylic nitrogen is bonding site.

EXPERIMENTAL

Materials: All the substance in this investigation were reagent grade (Aldrich). Schiff bases were prepared by the condensation of aldehydes with the same mol number of allylamine in methanol as reported earlier (Tiollois, 1962). Schiff bases are obtained as liquid in methanol. This was confirmed by the colour change of the solution. Schiff base have taken from methanol in rotary evaporator at 30°C. Reaction mechanizm of Schiff bases (Zlatkis, 1973):
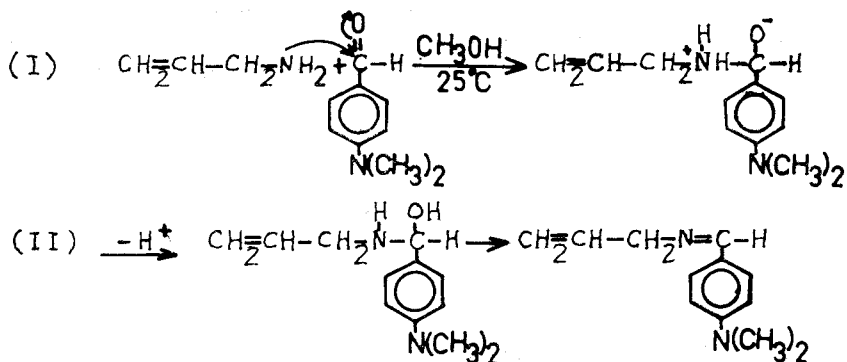

Synthesis of metal complexes: All the complexes were prepared by adding calculated amount of Schiff base to the metal salt in methanol at room temperature.

Metals: Th $(NO_3)_4$. $4H_2O$, UO_2 $(NO_3)_2$. $6H_2O$, $SnCl_4$. $5H_2O$, $SnCl_2$. $2H_2O$ Reaction mixture refluxed 15 minutes and NaOH solution was added untill the complex precipitate. Coloured solid complex was filtered and dried in vacuum dessicator.

Solid complexes were analysed for their carbon, nitrogen and hydrogen contents and results are recorded in table 1.

Table 1

Complex	Formula	% C		% N		% H	
		found	calc	found	calc	found	calc
(SB₁) UO₂(II)	$(UO_2C_{40}H_{40}N_{10}O_{14})$	40.1	41.59	11.92	12.13	3.25	3.46
(SB₁) Th (IV)	$(ThC_{40}H_{40}N_3O_8)\,OH_4$	44.20	45.28	10.11	11.56	3.70	4.15
(SB₁) Sn (IV)	$(SnC_{20}H_{20}N_4O_4Cl_4)$	37.1	37.46	8.1	8.74	2.96	3.12
(SB₂) UO₂(II)	$(UO_2C_{44}H_{48}N_2O_6)$	49.15	50.26	11.9	12.21	5.15	5.28
(SB₂) Th (IV)	$(Th\,C_{64}H_{48}N_6)\,OH_4$	53.25	54.75	10.15	10.64	6.02	6.46
(SB₂) Sn (IV)	$(SnC_{32}H_{24}N_4Cl_4)$	44.0	45.23	8.5	8.79	4.8	5.02
(SB₂) Sn (II)	$(SnC_{32}H_{24}N_4Cl_3)$	45.0	46.1	8.5	8.97	4.92	5.12

SB$_1$ $CH_2\!\!=\!\!CH\!-\!CH_2\!-\!N\!=\!C\!-\!H$

SB$_2$ $H\!-\!C\!=\!N\!-\!CH_2\!-\!CH\!=\!CH_2$
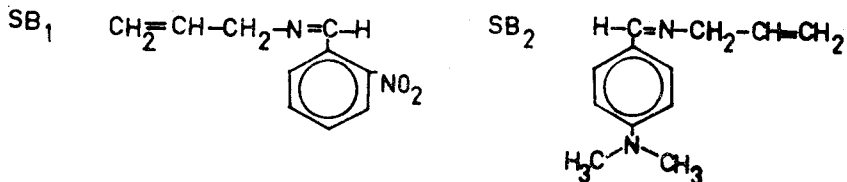
Magnetic susceptibility measurement were made by Gouy balance and results are recorded in table 2

Table 2

Complex	Gram susceptibility of complex
(SB$_1$) UO$_2$(II)	X_g— 7,05 10^{-7}(erg gauss^{-2})g^{-1}
(SB$_1$) Th (IV)	X_g— 6,92 10^{-7}(erg gauss^{-2})g^{-1}
(SB$_1$) Sn (IV)	X_g— 7,24 10^{-7}(erg gauss^{-2})g^{-1}
(SB$_2$) VO$_2$(II)	X_g— 1,04 10^{-6}(erg gauss^{-2})g^{-1}
(SB$_2$) Th (IV)	X_g— 5,14 10^{-7}(erg gauss^{-2})g^{-1}
(SB$_2$) Sn (IV)	X_g— 6,94 10^{-7}(erg gauss^{-2})g^{-1}
(SB$_2$) Sn (II)	X_g— 5,92 10^{-7}(erg gauss^{-2})g^{-1}

IR spectrum of the complexes have taken with Perkin-Elmer double beam spectrophotometer in nujol. N.M.R spectrum of Schiff bases have taken with Varian T 60 A spectrometer in CDCl$_3$. Electronic spectra of Schiff bases were measured with Hithachi model spectrophotometer using 1 cm matched quartz cell. Mass spectrum of the Schiff bases have taken with Fenningen Nat 1020 mass spectrometer and molecular weights were recorded as expected.

RESULT AND DISCUSSION

Characterization of Schiff bases were made by using N.M.R, IR and Mass spectrum. From N.M.R spectrum, it can be easly seen that there are six kinds of protons that have different chemical schifts. Aromatic protons observed at 7 and 8 ppm as double doublet, -N (CH$_3$)$_2$protons have peak at 3,1 ppm as singlet, terminal hydrogens at 5,05 ppm as triplet, aldehyde hydrogen at 8,5 ppm, a multiplet at 6,5 ppm and doublet at 4,20 ppm which belong to -N-CH$_2$-protons (Parikh, 1974 Functional group peaks are observed on IR spectrum. -NH (CH$_3$)$_2$ peaks are observed at 1260-1380 cm^{-1}, C$=$N

peak is at 1640 cm^{-1} and aromatic, alifatic CH stretching peaks at at 3080 and 2800 cm^{-1}. Absorption spectrum of Schiff bases also have taken and three peaks are observed at 377 nm, 333 nm and 250 nm which are resulted from n $\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ conjugation transitions.

Eight complexes were prepared from two Schiff bases and to explain the structure of these complexes, their IR spectra have been taken. In all complexes donor atoms are imine nitrogen. It is observed that C$=$N peak which is observed at 1640 cm^{-1} disappeared in complex (Mahmoud, 1980) This is resulted from bonding of nitrogen to metal atom. Thus, disappearance of the strecth of C$=$N on complexation is due to the decrease in electron density within this band as a result of high positive charge of coordinated metal ion.

From this study, we concluded that:

i) All the ligands (Schiff bases) are monodentate and imine nitrogen is bonding site.

ii) All the complexes are diamagnetic.

iii) They have very high melting points.

iv) They are insoluble in CCl$_4$, CHCl$_3$, pyridine, acetone, CS$_2$, DMSO, H$_2$0, benzene and dioxane.

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