Grafting of the Acrylic Acid on Poly(ethylene Terephthalate)

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Synopsis

A study has been made of the effect of solvent nature, concentrations of monomer, initiator and homopolymerization inhibitors, and initial polymer structure on the modification of poly(ethylene terephthalate) (PET) films and fibers by grafting the acrylic acid (AA). AA grafting initiated by radicals formed from thermal decomposition of benzoyl peroxide. It has been established that preswelling of PET in dichloroethane leads to changes in its sorption–diffusion properties and favors an increase in the degree of grafting. Addition of the Fe(II), Ni(II), and Cu(II) salts to AA solution decreased homopolymer yield. The studied process of grafting can be described by equations of diffusion kinetics. Distribution of the poly(acrylic acid) (PAA) over the cross section of samples and a number of physical and chemical properties depend also on conditions of performing the graft polymerization.

INTRODUCTION

The grafting of AA to PET films and fibers makes it possible to improve their hydrophilicity, dyeability, adhesion, and antistatic properties.[1] It is of considerable importance that due to this method the PET obtains cation exchange properties. As a result, the PET–PAA films can be used as ion-exchange membranes while PET–PAA fibers can be used for chemosorption. However, the grafting of vinyl monomers on PET meets with some difficulties. First, the chemical structure of PET hinders considerable concentration of radicals for initiating grafting (in particular, as reported by Sakurada and co-workers,[2] under the effect of high-energy radiation). Second, high crystallinity of industrial PET samples and highly ordered macromolecules in amorphous regions hinder monomer diffusion inside the material[3] and limit a grafting zone to subsurface regions. Besides, homopolymerization inhibits effective grafting. Therefore, in spite of the application of different initiation methods (γ-radiation, peroxidation, and redox systems) and variation of grafting conditions, the authors of a number of works devoted to this problem[4-7] failed to obtain high grafting degrees.

The present paper considers physicochemical regularities on the AA grafting on PET films and fibers initiated by radicals formed from thermal decomposition of benzoyl peroxide. The dependence of cation exchange capacity, hydrophility, dyeability, mechanical, and thermal stability of materials obtained on the PAA content and its distribution over cross section have been also studied.

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EXPERIMENTAL

As initial materials, an undrawn PET film "lavsan" of thickness 220–250 μm and PET fiber "lavsan" (diameter 10 μm, drawing ratio 3) were used. Before grafting, the orientation of films was carried out by stretching in water at 353 K to obtain the required drawing ratio, λ. The AA was purified by distillation under the pressure of 50 hPa; benzoyl peroxide, by recrystallization from solution in chloroform. 1,2-Dichloroethane of grade "pure" and dyes, Rhodamin C, Methylene Blue, and Dispersed Blue, were applied without additional purification.

Grafting

Before grafting, the samples of PET films and fibers were placed into a 5% solution of benzoyl peroxide in toluene for 15 min. When preswelling was performed, the samples were treated in dichloroethane at 293 K for 1–60 min. After toluene had been evaporated, the samples were placed into the ampoules with AA solutions. The concentration of AA aqueous solutions was varied in wide ranges (most often the concentration of 2 M/L was used). The PET/AA mass ratio w was controlled. To inhibit homopolymerization, inhibitors were added into the solution. The polymerization time τ was 1–6 h at 353 K. After heating, the homopolymer was washed off with boiling water for 6 h and the samples then were dried at 373 K to a constant mass. The degree of grafting ΔM, AA conversion Q, and grafting efficiency E were calculated according to the following equation:

$$\Delta M = \frac{M_1 - M_0}{M_0} \cdot 100\% \tag{1}$$

$$Q = \frac{M_2 + M_3}{M} \cdot 100\% \tag{2}$$

$$E = \frac{M_2}{M_2 + M_3} \cdot 100\% \tag{3}$$

where M_0 = sample mass before grafting, M_1 = sample mass after grafting and washing the homopolymer, M_2 = grafted PAA mass, M_3 = PAA homopolymer mass, and M = AA mass.

Determination of Dyeability and PAA Distribution over Cross Section

In dyeability studies the basic and dispersed dyes were used. A weight amount of fiber (0.2 g) was placed into an aqueous solution or suspension of dye (100 mL, 0.2 g/L) and allowed to stand for 2 h at 373 K. The fibers then were twice washed with water for 1 h at 373 K. A dyeability value, Δm, was found by use of photoelectrocolorimeter from the difference between dye quantities, sorbed by the fiber during dyeing and extracted upon washing. It was expressed in grams of dye per 1 gram of fiber. To study the nature of PAA distribution over cross section, the films were dyed under similar conditions

with Rhodamine C, which was fixed on acidic groups of the polymer. Film cross sections were investigated with an optical microscope.

Determination of Cation Exchange Capacity and Moisture Sorption

The total cation exchange capacity (CEC) was determined according to $0.1N$ NaOH. Moisture sorption ω was found at pH 7. Standard techniques were used.[8] An average quantity of water molecules associated with one carboxyl group of a swollen polymer, n, was calculated from the equation

$$n = \frac{\omega \cdot 1000}{\text{CEC} \cdot M_{H_2O}} \tag{4}$$

where ω is moisture sorption, mass of water (g) per 1 g polymer, CEC is total cation exchange capacity, meq/g, and M_{H_2O} is water molecular mass.

RESULTS AND DISCUSSION

Two methods of introduction of the initiator into a reaction medium were compared. They are saturation of PET in toluene solution with initiator added and the direct introduction of initiator into polymerization solution. It has been shown that under otherwise equal conditions, the grafting degree was higher in the former than in the latter case. For instance, at $\tau = 1$ h and [AA] = 1.5 M/L, the values of ΔM vary from 23 to 8%, respectively. In our opinion, such a regularity is explained both by preferential accumulation of radicals being formed at benzoyl peroxide decomposition in the polymer phase and higher efficiency of benzoyl peroxide decomposition between polymer structure elements. Such efficiency is a result of immobilization of radicals with walls, which increases the probability of formation of polymer radicals.[9] However, it is required that further grafting be carried out from the solution not extracting benzoyl peroxide from PET. Therefore, it is appropriate to use water as an AA solvent in the process under investigation.

The value of ΔM is function of [AA] (Fig. 1). A decrease in ΔM and E observed at [AA] > 3 M/L is a result of simultaneous increase in the homopolymerization rate with growing [AA] which leads to depletion of the monomer. In addition, the homopolymer accumulated increases the reaction medium viscosity, which inhibits the AA diffusion toward growing polymer chains. In this respect further experiments were run at [AA] = 2 M/L.

The possibility of increasing M and E by deactivation of low-molecular radicals inducing AA homopolymerization has been studied. In this case, the inhibitors applied upon radiation-induced grafting were used (Table I). Organic inhibitors at 5–20 mM/L have been found to suppress both homopolymerization and grafting. The best result was achieved with Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ at concentration of 10–15 mM/L (Fig. 2). The curves, presented in Figure 2, can be explained by action of Fe^{2+} ions, which at low concentrations partially migrate into a polymer, thereby deactivating mainly low-molecular radicals formed at the solution/polymer interphase. However, at higher concentrations of Mohr's salt, a quantity of Fe^{2+} ions
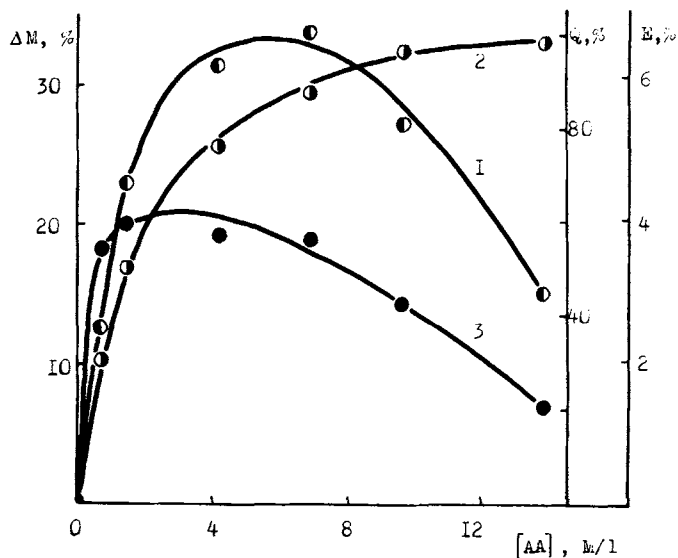
Fig. 1. Dependence of grafting degree (1), AA conversion degree (2), and efficiency (3) of AA grafting to PET films on AA concentration ($\tau = 1$ h, $w = 0.15$).

diffusing into the polymer phase increases. As a result, they start deactivating macroradicals to a greater extent hindering the generation and growth of graft chains. Besides, since Fe^{2+} ions accelerate the benzoyl peroxide decomposition, their high concentration favors the rapid initiator consumption.

To provide a high yield of the graft PAA, a considerable concentration of macroradicals is required during reaction, the grafting temperature (353 K)

TABLE I
Effect of Inhibitors on Grafting and Homopolymerization of Acrylic Acid[a]

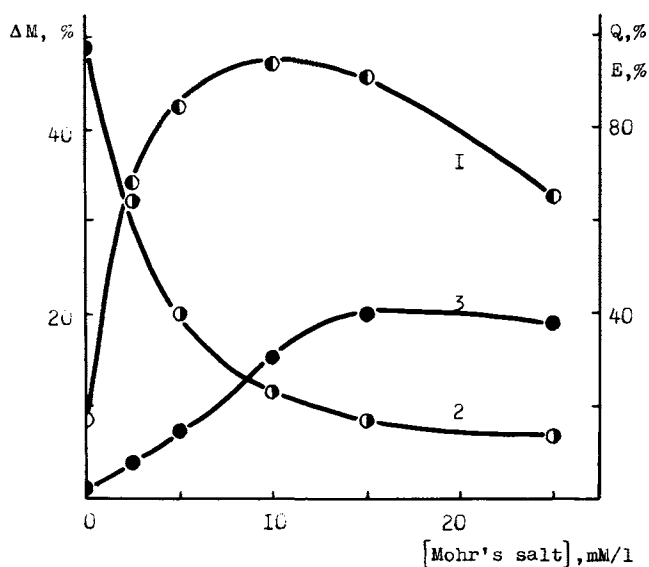| Inhibitor	Concentration (mM/L)	$\Delta M(\%)$	$Q(\%)$	$E(\%)$
—	0	8	99	1
Hydroquinone	25	0.5	2	4
	10	2	2	15
	5	4	15	19
Pyrogallol	10	2	2	15
p-Metoxiphenol	10	2	1	30
$CuCl_2$	10	18	6	45
$CuSO_4 \cdot 5H_2O$	10	19	8	36
$FeSO_4 \cdot 7H_2O$	25	32	14	34
	10	43	23	28
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	25	32	13	37
	10	47	23	21
	2.5	34	65	8
$NiCl_2 \cdot 6H_2O$	25	29	10	44
	10	40	26	23

[a]([AA] = 2 M/L, $w = 0.15$, $\tau = 1$ h.)

Fig. 2. Dependence of grafting degree (1), AA conversion degree (2), and efficiency (3) of AA grafting to PET films on Mohr's salt concentration ([AA] = 2 M/L, τ = 1 h, w = 0.15).

being chosen in the course of the experiment with allowance for kinetic characteristics of thermal benzoyl peroxide decomposition.[10]

The grafting rate and value of ΔM are affected by treatment of the initial films and fibers with dichloroethane (Fig. 3). Such an effect appeared to be more efficient than introduction of the dichloroacetic acid and benzyl alcohol
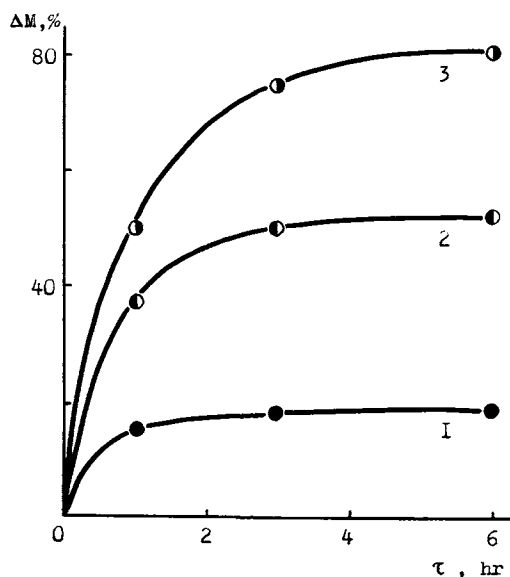

Fig. 3. Kinetic curves of PAA accumulation upon grafting to an undrawn PET film without (1) and with (2) dichloroethane during 1 and 60 min (3) at 293 K.
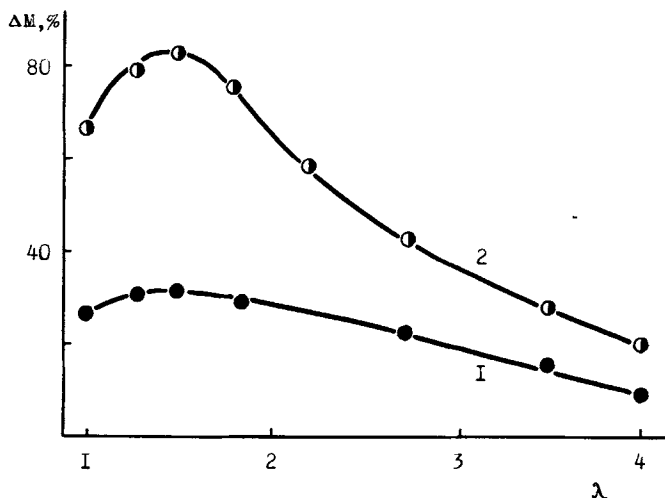
Fig. 4. Dependence of ΔM on λ of PET films without (1) and with (2) dichloroethane during 60 min at 293 K.

into solution of monomer applied in works.[3,7] It has been established that the treatment with dichloroethane stimulates benzoyl peroxide and AA sorption and diffusion. So, after swelling in a 5% toluene solution of benzoyl peroxide, the initial PET film contains 1.5% of the latter. Under similar conditions, a film, pretreated with dichloroethane, sorbs as 4% of benzoyl peroxide. The initial PET film sorbs up to 6% of AA at 293 K while a film treated with dichloroethane, up to 12%. In this case an sorption rate increases. As a result, the probability of formation of graft chains over the whole material volume increases. A monomer concentration in the grafting zone remains considerable due to improvement of the AA diffusion.

The dependence of a grafting degree on the initial PET drawing ratio is of extreme character (Fig. 4). An increase in ΔM with λ as high as 1.5 can be explained by straightening a part of macromolecules in amorphous regions and increasing a free volume fraction. These changes promote the AA and benzoyl peroxide sorption, as well as make it possible to accumulate considerable quantities of PAA in interlamellar regions. As a result of drawing, film thickness is also decreased. It is followed by an increase in their specific surface and decrease in a fraction of internal regions that are almost accessible for a sorbate.

The optical-microscopic analysis of film cross sections showed that upon grafting on undrawn PET without dichloroethane, the PAA is localized in subsurface layers. The graft layer thickness depends on ΔM and is 10–40 μm. However, when dichloroethane was used, the 17% PAA grafting provides a high concentration of carboxylic groups throughout the thickness of the films. The observed PAA behavior agrees with estimations of the characteristic graft polymerization parameter α according to the diffusion-kinetic equation

$$\alpha \, th \, \alpha = VL^2/4[AA]_0 D \qquad (5)$$

connecting the grafting rate V with the material diffusion characteristics —equilibrium monomer concentration $[AA]_0$ and diffusion coefficient D (L is
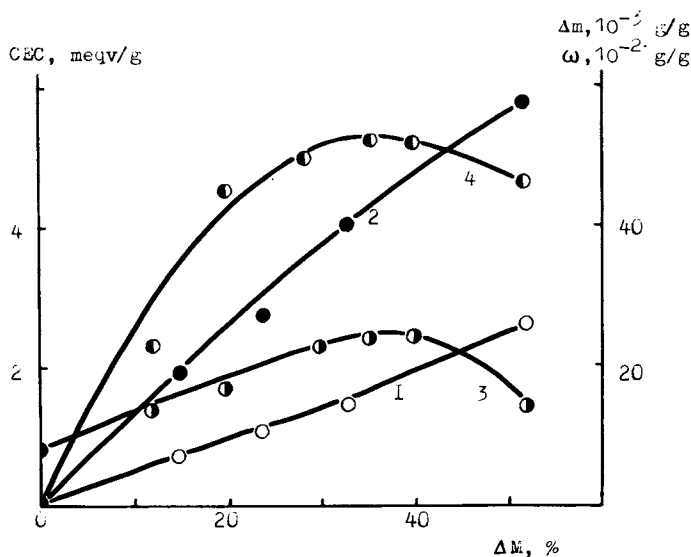
Fig. 5. Dependence of moisture sorption (1), CEC (2), sorption of disperse blue (3), and methylene blue (4) on the PET–PAA graft fiber content.

film thickness).[11] In the case of grafting, when dichloroethane was used, $\alpha < 4$. It is indicative of a reaction proceeding under diffusion-kinetics conditions as opposed to grafting without dichloroethane when $\alpha > 4$. It corresponds to the diffusion condition according to Ref. 12. The PAA distribution over the cross section of predrawned PET films treated with dichloroethane depends on λ. When $\lambda \leq 2$, the PAA is distributed through the whole volume while at $\lambda \geq 2.5$ it is localized at the surface.

As a result of grafting, the tensile strength of films decreases by 10–20% amounting to 120–140 MPa at $\Delta M = 15$–75% and $\lambda = 3$. The grafting on an undrawn film of 75% PAA increases a yield temperature from 530 to 600 K. Upon grafting on predrawn films, the subsurface layers enriched with PAA provide higher thermostability of materials at lower values of ΔM.[13]

The moisture sorption and CEC of PET–PAA increase with grafting degree (Fig. 5). An average number of water molecules associated with one carboxylic group of the swollen copolymer at pH 7 changes from 2.0 at $\Delta M = 15\%$ to 3.2 at $\Delta M = 76\%$. The hydrogen substitution rate in carboxylic groups at ion exchange also increases with ΔM (Fig. 6). CEC does not depend on the PAA distribution through a volume.

A sorption degree of dyes with modified fibers increases with ΔM of PAA as reported in Refs. 4 and 7 too. However, a further increase in the grafting degree (after $\Delta M = 40\%$) decreases dyeability (Fig. 5). The latter fact indicates that upon grafting over 40% PAA, the dye sorption is rather affected by progressing filling of a free fiber volume with PAA microstructures and formation of a spatial net that hinder the diffusion of dyes. The dependence of sorption degree of dyes on a PAA grafting degree, its extreme nature, is similar to that of strain–stress and thermal properties on ΔM of PET–PAA copolymers.[14] The dyeability with Methylene Blue at $\Delta M > 40\%$ also starts decreasing despite an increase in concentration of carboxylic groups. It sug-

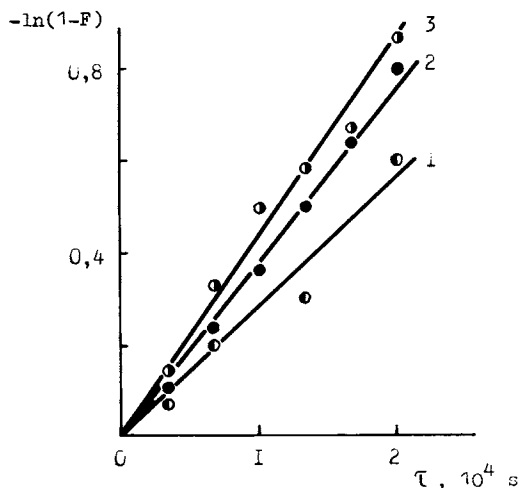Fig. 6. H^+–Na^+ exchange kinetics in the PET–PAA graft films from $0.1N$ NaOH solution [F = exchange degree; ΔM PAA: (1) 18%; (2) 41%; (3) 72%].

gests that the function of a fiber structure is also important upon volume dyeing with the basic dyes.

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