

Introduction of Quaternary Amines onto a Film Surface by Graft Polymerization

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SYNOPSIS

Quaternary amines were introduced onto a poly(ethylene terephthalate) (PET) film surface by two different methods using UV-induced graft polymerization. The first involves a two-step reaction: graft polymerization of *N,N'*-(dimethylamino)ethyl methacrylate (DMAEMA) onto the PET film, followed by quaternization of the tertiary *N,N'*-dimethylamino groups of grafted chains using alkyl bromides ($R_n\text{Br}$). The second is direct graft polymerization of DMAEMA having pendant quaternary amines onto the PET film. The alkyl bromides used for quaternization of the monomers and graft chains include: *n*-propyl, *n*-butyl, *n*-octyl, *n*-lauryl, and *n*-cetyl bromide. The two-step method could quaternarize 90% of the pendant *N,N'*-dimethylamino groups of the graft chains when $R_3\text{Br}$ was used. The extent of quaternization decreased with the increasing carbon number of alkyl bromide. The direct one-step method gave a graft amine density of 8 nmol/cm² when the monomer quaternized with $R_3\text{Br}$ was used for the graft polymerization in the presence of $1 \times 10^{-3}M$ sodium metaperiodate. The carbon number of alkyl chains in the quaternary amines estimated from XPS spectra was in good agreement with that of $R_n\text{Br}$ used for quaternization. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A number of methods have been applied for surface modification of polymers, including chemical oxidation, discharge with plasma, surface coating, metalizing, graft polymerization, crosslinking, etching, and so on. Most of them are associated with problems such as efficacy, durability, and processing cost. The durability of polymer surfaces modified by graft polymerization is generally better than that of oxidation and coating, since macromolecular chains produced by graft polymerization are covalently immobilized onto the surface of polymer substrates. Recently, numerous studies have been performed to modify polymer surfaces by graft polymerization of nonionic monomers such as acrylamide,¹ acrylonitrile,² dimethylacrylamide,³ and glycidyl methacrylate,⁴ or of anionic monomers such as acrylic acid,^{1,5}

2-acrylamido-2-methyl-propanesulfonic acid,⁶ and 4-styrenesulfonic acid.¹ On the contrary, fewer studies have been devoted to surface graft polymerization of cationic monomers, mostly tertiary amines.^{5,7} Since the degree of dissociation of tertiary amines readily varies with pH of solution, resulting in vanishing of the cationic character at high pH, the graft chains should carry quaternary amines to maintain the stable cationic character over a wide pH range. Although some attempts have been made to introduce quaternary amines into polymer chains, in particular in the field of antimicrobial protection, most of them are crosslinking with alkoxy silane,⁸ blending,^{9,10} and coating¹¹; which involve problems such as poor durability during laundering and limited applicability. The surface modification using alkoxy silane needs hydroxyl groups on the polymers to be modified. Recently, quaternization of a nylon surface using dimethyl sulfate was reported for graft polymerization of *N,N'*-(dimethylamino)ethyl methacrylate (DMAEMA).¹²

The present study was undertaken to introduce quaternary amines having different lengths of alkyl

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group onto a poly(ethylene terephthalate) (PET) film with two different methods, as illustrated in Figure 1. Both methods make use of UV-induced graft polymerization.¹³

EXPERIMENTAL

Film and Reagents

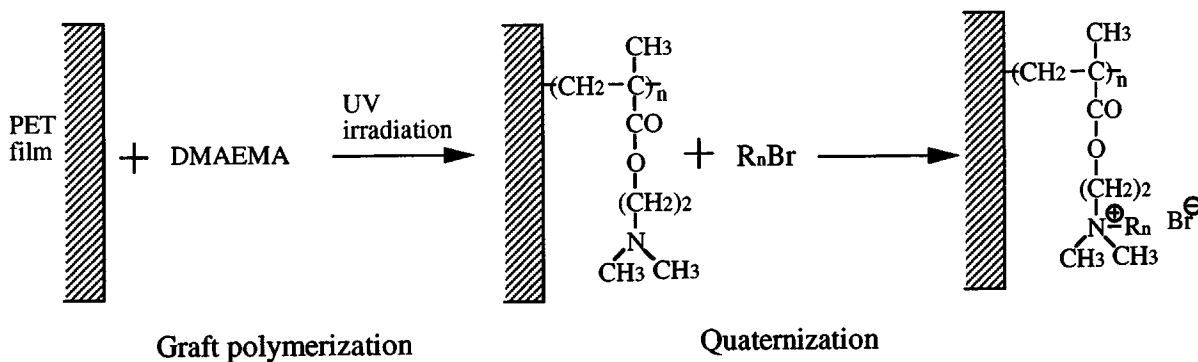
A biaxially oriented PET film of 50 μm thickness was kindly provided by Teijin Co., Ltd., Tokyo, Japan. For purification, it was subjected to Soxhlet extraction with methyl alcohol for 20 h. The tertiary amine monomer used throughout this work was DMAEMA (Mitsubishi Gas Chemical Co., Ltd., Tokyo, Japan). Alkyl bromides ($R_n\text{Br}$) with different alkyl chain lengths [*n*-propyl ($R_3\text{Br}$), *n*-butyl ($R_4\text{Br}$), *n*-octyl ($R_8\text{Br}$), *n*-lauryl ($R_{12}\text{Br}$), and *n*-cetyl ($R_{16}\text{Br}$)] were used for quaternization. Acid Orange 7 (Tokyo Kasei Co., Ltd., Tokyo, Japan, λ_{max} 485 nm) was

purified using the Robinson-Mills method. Meta-sodium periodate (NaIO_4) and $R_n\text{Br}$ as well as other reagents of extra-pure grade were used as obtained.

Preparation of Quaternary Amine Monomers

Quaternary amine monomers were derived from the tertiary DMAEMA monomer using a series of alkyl bromides. Briefly, the mixture of DMAEMA and $R_n\text{Br}$ (2 : 1, by mole) was stirred for two days at room temperature and then the products were separated from the mixture. White and nearly odorless powders were obtained when the products were washed with ethyl acetate in excess and vacuum-dried. The powders were freely soluble in ethyl alcohol, easily soluble in water, and slightly soluble in acetone except for the propyl and cetyl derivatives. Their characterization was performed by NMR with JNM-PMX60SI using tetramethyl silane as an internal standard in deuteriochloroform. Referring to Sadtler standard NMR spectra, the

Two-step method



One-step method

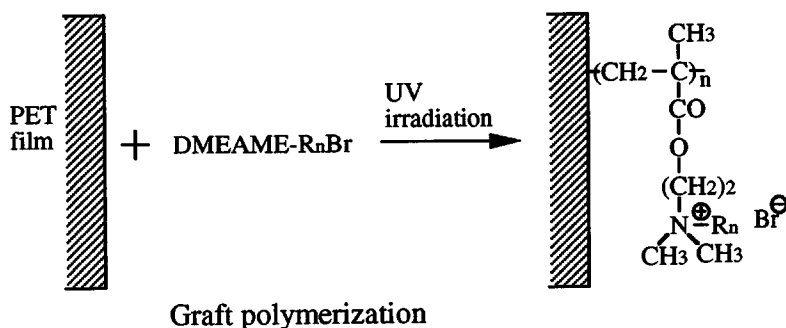


Figure 1 Two methods for quaternization.

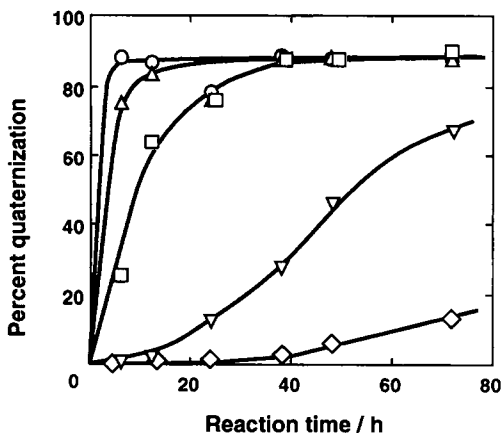


Figure 2 Effect of the reaction time and temperature on the quaternization of polyDMAEMA grafted film using $R_n\text{Br}$. Reaction temperature (\diamond); 4°C, (∇); 20°C, (\square); 37°C, (Δ); 50°C, and (\circ); 60°C.

peak at 1.3 ppm was assigned to the alkyl chain in the alkyl bromide ($-(\text{CH}_2)_{n-1}-\text{CH}_3$). The signal strength was proportional to the alkyl chain length, indicating that quaternary amine monomers could be produced by derivation of the tertiary amine monomers with alkyl bromides. Hereafter, these quaternized monomers are called DMAEMA- $R_3\text{Br}$, DMAEMA- $R_4\text{Br}$, DMAEMA- $R_8\text{Br}$, DMAEMA- $R_{12}\text{Br}$, and DMAEMA- $R_{16}\text{Br}$.

Graft Polymerization

Graft polymerization of the tertiary and quaternary amine monomers onto the PET film was performed with the simultaneous UV irradiation method without photosensitizer and degassing.¹³ Briefly, strips of PET film were placed in a Pyrex glass ampoule containing an excess of the aqueous monomer solution containing NaIO_4 . The film and the monomer mixture in the ampoule were exposed to UV radiation from a 1000 W high-pressure mercury lamp (2537–5791 Å Riko rotary RH400-10 w type, Riko Co., Ltd., Tokyo, Japan). After UV irradiation, the films were placed in plenty of distilled water under continuous stirring for longer than 20 h at 25°C to remove the homopolymer.

Quaternization of Tertiary Amine on the Grafted Chains

Tertiary amine grafted PET films were placed in an excess of alkyl bromide for a predetermined time and then placed in ethyl alcohol to remove the un-

reacted alkyl bromide, followed by washing with double distilled water.

Characterization of Modified Surface

XPS spectra were recorded with a Spectrometer ESCA 850 manufactured by Shimadzu Corp., Kyoto, Japan. A magnesium-anode source producing $\text{MgK}\alpha$ X-ray at 8 kV and 30 mÅ was used and the pressure in the instrument was maintained at 5×10^{-5} Pa. The angle of incident X-rays to the film surface was fixed to 90°.

Zeta potentials of grafted PET films were measured as a function of pH by a streaming potential method using the cell unit described elsewhere.¹⁴ The electrode was made of platinum and the streaming potential, E , was recorded by an automatic X-Y plotter as a function of the pressure difference, P . The zeta potential, ζ , was calculated by the relation:

$$\zeta = (4\pi\eta\lambda/\varepsilon)(E/P) \quad (1)$$

where η and ε are the viscosity and the dielectric constant of the solution, respectively, and λ is the specific conductance of the solution. The pH values were measured using a Hitachi-Horiba pH meter of type F-5 and the ionic strength of the electrolyte solution used for the potential measurement was kept to 1×10^{-3} by the use of KCl.

PET films were dyed with Acid Orange 7 in a refluxed bath at $5 \times 10^{-4}M$ dye concentration and 50°C for 30 min. Except for the study on the effect of pH change, dyeing was conducted at pH 3, which was adjusted with HCl without any other electrolyte. After dyeing, the optical density of the film was

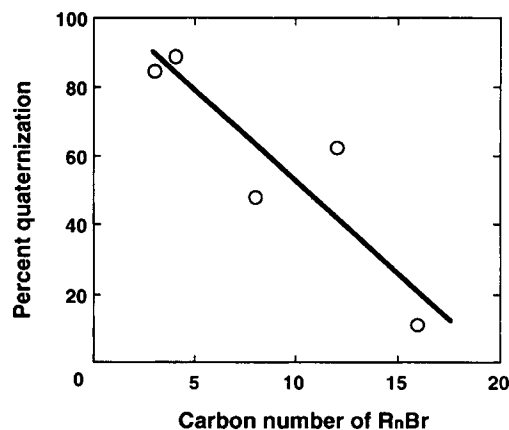


Figure 3 Effect of the carbon number of $R_n\text{Br}$ on the quaternization of polyDMAEMA grafted film.

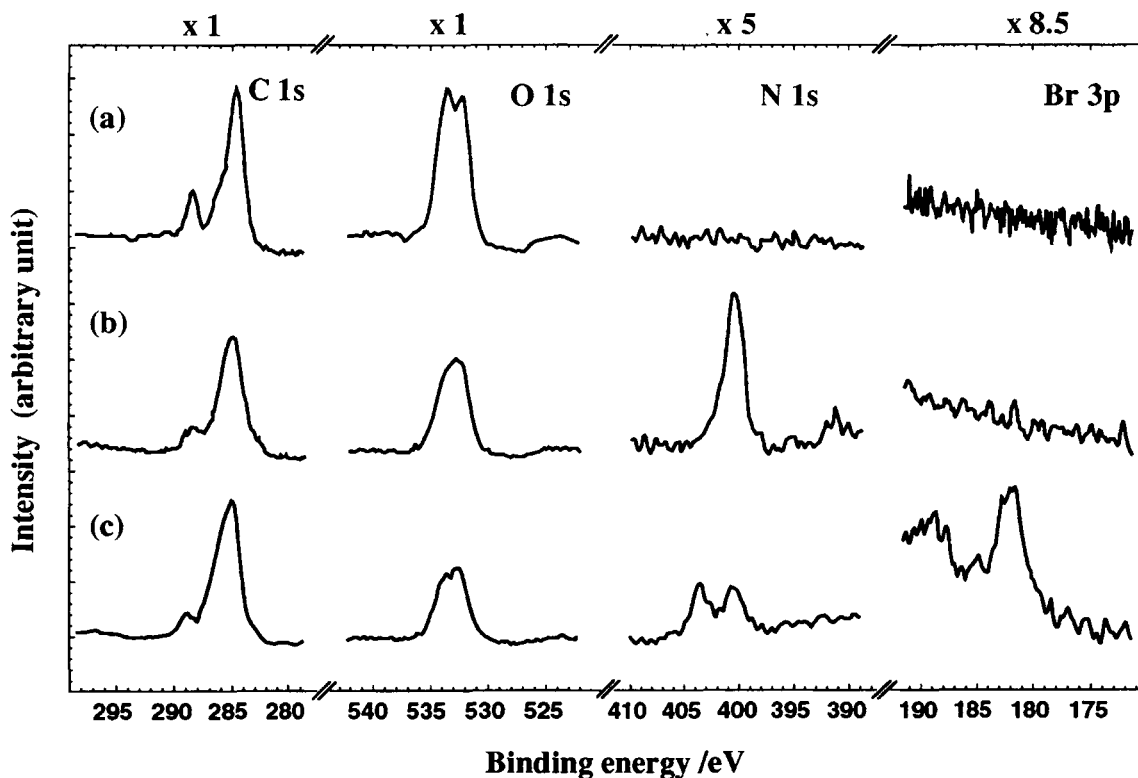


Figure 4 XPS spectra of the virgin PET film (a), polyDMAEMA grafted PET film (1 wt % monomer, $5 \times 10^{-4} M$ NaIO_4 , 27°C , and 1.5 h) (b), and the grafted PET film quaternized using R_3Br at 50°C for 20 h (c).

measured with a spectrophotometer (Hitachi 200-20) at 485 nm.

RESULTS

Two-Step Quaternization

As the first step of quaternization, graft polymerization of DMAEMA was carried out by UV irradiation of the film in the presence of monomer and NaIO_4 in an aqueous medium, as described elsewhere.⁷ The resulting polyDMAEMA grafted film with a fixed graft density of 50 nmol/cm^2 was used for the quaternization of the polyDMAEMA graft chains with R_nBr throughout this work. If the polyDMAEMA chains are thoroughly quaternized with R_3Br , the surface density of the quaternary amine on the grafted PET film will reach 50 nmol/cm^2 .

Figure 2 shows effects of the reaction time and temperature on the quaternization of $-\text{N}(\text{CH}_3)_2$ groups in the polyDMAEMA graft chains when R_4Br was used for the reaction. It is apparent that quaternization takes place more rapidly at higher

reaction temperature, being saturated around 90%, irrespective of the reaction temperature. The quaternization with R_nBr at 50°C for 20 h produced the result shown in Figure 3. As is seen, the percent quaternization decreases with the increasing chain length of R_nBr . When cetyl bromide (R_{16}Br) was used for the quaternization of polyDMAEMA graft chains, only 10% of the $-\text{N}(\text{CH}_3)_2$ group was converted to the quaternary amine under this reaction condition.

Figure 4 shows XPS spectra of the virgin PET film, the polyDMAEMA grafted PET film, and the grafted film quaternized using R_3Br . The O 1s, N 1s, and Br 3p intensities were normalized concerning the C 1s intensity. The spectra of the virgin PET film are in full agreement with those published in literature.¹⁵⁻¹⁷ The area ratio of carbon peaks obtained by curve fitting into three C 1s photo peaks is 62 : 21 : 17 (not shown here), being nearly identical with the theoretical value (60 : 20 : 20). The ratio of oxygen peaks is also in good agreement with the theoretical. Graft polymerization of the tertiary amine DMAEMA produced a new peak in the N 1s spectrum, while another new peak ap-

Table I Estimation of the Carbon Number of Alkyl Chains in the Quaternary Amines from XPS Spectra for polyDMAEMA Grafted Films Quaternized Using a Series of $R_n\text{Br}$

Alkyl Bromide	Atomic Concentration/mole %				Calc. Carbon Number of the Alkyl Chain
	C1s	O1s	Br 3p	N1s	
$R_3\text{Br}$	73.0	16.8	3.7	6.5	3.1
$R_4\text{Br}$	74.5	15.3	4.2	6.0	4.4
$R_8\text{Br}$	75.2	17.8	1.9	5.2	8.1
$R_{12}\text{Br}$	78.5	14.7	2.1	4.7	13.2
$R_{16}\text{Br}$	78.0	16.3	1.0	4.7	22.7

peared in the Br 3_p spectrum after quaternization of the grafted film with $R_3\text{Br}$. This provides evidence for quaternization of $-\text{N}(\text{CH}_3)_2$ groups existing on the grafted PET film. However, the presence of two peaks (tertiary and quaternary amine at 401.2 eV and 403.7 eV) seen in the N1s spectrum indicates that quaternization was not complete. The atomic concentration of each signal for the films quaternized using a series of $R_n\text{Br}$ and the carbon number of alkyl chains in the quaternary amine estimated from the atomic concentrations is shown in Table I. The estimation of the carbon number was made in the following manner. As 1 mol of the repeating unit of polyDMAEMA chain contains 1 mol of $-\text{N}(\text{CH}_3)_2$, C=O, and C—O—C, the concentration of O1s([O1s]) in 1 mol of the repeating unit is obtained by doubling [N1s]. Thus, [C1s] in each component is calculated from eqs. (2–4).

[C1s] in the PET component

$$= \{(\text{total [O1s]} - [\text{N1s}] \times 2)/4\} \times 10 \quad (2)$$

[C1s] in the quaternized graft chain component

$$= \text{total [C1s]} - [\text{C1s}]$$

in the PET component (3)

[C1s] in the alkyl chain component

$$= [\text{C1s}] \text{ in the quaternized graft}$$

chain component $-[\text{N1s}] \times 8 \quad (4)$

Then, the carbon number of the alkyl chain in the quaternary amine can be obtained by dividing [C1s] in the alkyl chain component by [Br 3_p]. The estimated carbon numbers are given in Table I. Ob-

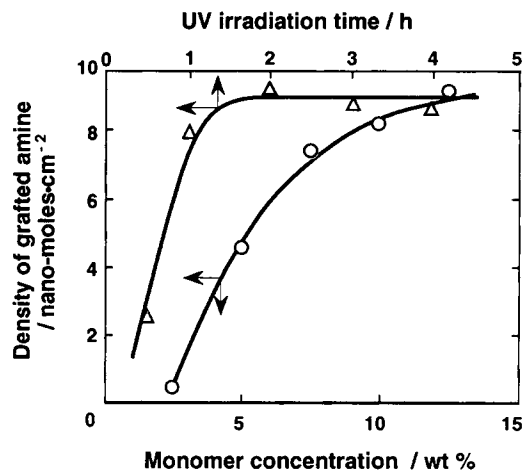


Figure 5 Effect of the monomer concentration and the UV irradiation time on the graft polymerization of DMAEMA- $R_3\text{Br}$ monomer onto PET film (10 wt % monomer, 40°C, and 3 h).

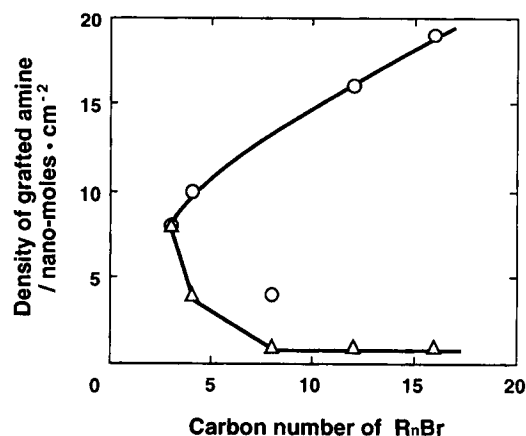


Figure 6 Graft polymerization of DMAEMA- $R_n\text{Br}$ monomer onto PET film (10 wt % monomer, $1 \times 10^{-3}M$ NaIO_4 , and 3 h). Reaction temperature (Δ); 20°C and (\circ); 40°C.

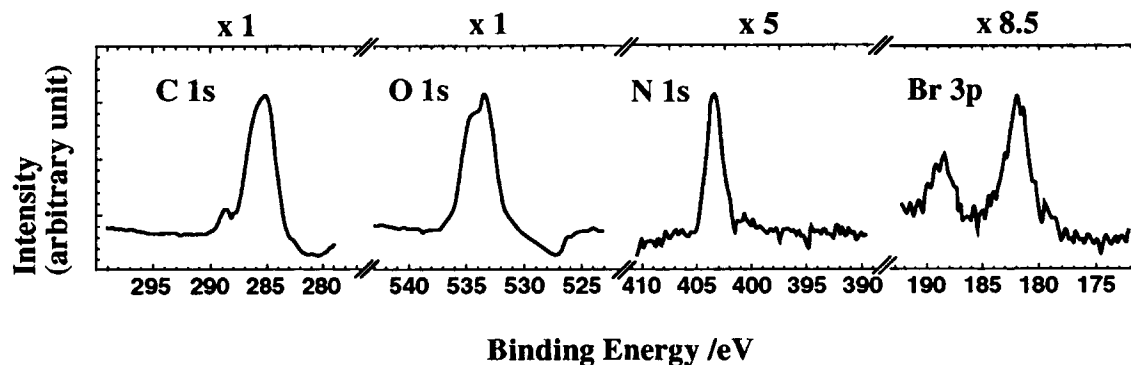


Figure 7 XPS spectra of polyDMAEMA- R_3 Br grafted PET film (10 wt % monomer, $1 \times 10^{-3}M$ $NaIO_4$, $40^\circ C$, and 3 h).

viously, the agreement with the carbon number of the R_n Br used for quaternization is satisfactory except for the film quaternized using R_{16} Br.

One-Step Quaternization

In this case, quaternized DMAEMA monomers (DMAEMA- R_n Br) were employed instead of the unquaternized DMAEMA used in the two-step quaternization. The virgin PET film was immersed in different concentrations of aqueous DMAEMA- R_n Br solutions containing $NaIO_4$ and exposed to UV radiation without degassing. The results obtained for graft polymerization of DMAEMA- R_3 Br are shown in Figure 5. The density of graft polymer chains increases with the increasing monomer concentration and UV irradiation time, leveling off at about 9 nmol/cm^2 when graft polymerization was carried out using 10 wt % monomer for 2 h and longer. Figure 6 shows the result of graft polymerization of monomers quaternized using a series of R_n Br. The graft polymerization was carried out with 10 wt % monomer containing $1 \times 10^{-3}M$ $NaIO_4$ at 20 and $40^\circ C$ for 3 h. For the graft polymerization at $20^\circ C$, the density of quaternary amine grafted

onto the PET film decreases with an increase in the alkyl chain length in DMAEMA- R_n Br. On the other hand, at $40^\circ C$ graft polymerization, the density of quaternary amine increases with the increasing monomer size except for the DMAEMA- R_8 Br.

XPS spectra of the polyDMAEMA- R_3 Br grafted PET film are shown in Figure 7. Clearly, graft polymerization of the quaternary amine monomer produced new peaks in the N1s spectrum characteristic of $-N(CH_3)_2$ and Br 3p spectrum characteristic of R_3 Br. The peak in the N1s spectrum (403.7 eV) is obviously different from that of the polyDMAEMA grafted PET film quaternized with R_3 Br after graft polymerization (Fig. 4). This suggests that the graft chains obtained by this one-step method contain only one kind of amine, that is, the quaternary amine. The atomic concentration of each signal of the films graft-polymerized with a series of DMAEMA- R_n Br and the carbon number of the alkyl chains in the quaternary amines estimated from the atomic concentrations by the same procedure as in the two-step method are shown in Table II. It is seen that the estimated carbon numbers are in good agreement with the theoretical, similar to the two-step quaternization.

Table II Estimation of the Carbon Number of Alkyl Chains in the Quaternary Amines from XPS Spectra for polyDMAEMA- R_n Br Grafted Films

Alkyl Bromide	Atomic Concentration/mol %				Calc. Carbon Number of the Alkyl Chain
	C1s	O1s	Br 3p	N1s	
R_3 Br	74.1	19.5	2.4	4.1	3.3
R_4 Br	73.2	22.4	2.0	2.4	4.2
R_8 Br	78.4	14.6	3.0	4.0	7.4
R_{12} Br	80.3	13.8	2.9	3.1	11.9
R_{16} Br	80.7	12.1	2.2	3.0	14.5

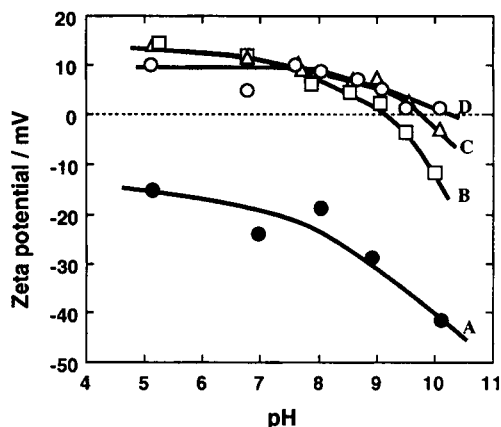


Figure 8 Effect of pH on the zeta potential of grafted PET films carrying introduced tertiary and quaternary amines (25°C, ionic strength of 1×10^{-3}). (●); A, (□); B (45 nmol/cm²), (Δ); C (90% quaternization), and (○); D (10 nmol/cm²).

Surface Properties of Graft Films Before and After Quaternization

A major difference between tertiary and quaternary amines is the dependence of their ionic dissociation on pH in the aqueous medium. To demonstrate this difference, we show the results obtained when R₃Br was used for the quaternization. Figure 8 shows the zeta potential dependence on pH for the virgin PET film (A), the polyDMAEMA grafted films before (B) and after (C) quaternization, and for the polyDMAEMA-R₃Br grafted film (D). Apparently, B and C show the same zeta potentials below pH 7 because of the same graft density and complete dissociation, but the zeta potential of B decreases steeply due to reduced dissociation at pH above 7.0. In contrast, the zeta potential of D decreases by only 10 mV when pH shifts from 5 to 10.

It is also expected that ionic binding of an anionic compound to the cationically grafted films will be greatly influenced by the extent of quaternization. To test this ionic binding, we chose Acid Orange 7 having one SO₃ group as the anionic compound, since the binding of Acid Orange 7 to cationic units in graft chains took place at a 1 : 1 molar ratio and the optical density of the film treated with the anionic dye was directly proportional to the amount of the dye extracted from the treated film.¹⁸ In this study, the films possessing quaternary amines introduced by the one-step and two-step quaternization were treated with Acid Orange 7 at pH from 2.5 to 12 and then the optical density was measured. Figure 9 shows the result. D_i and D_∞ are the optical

density of the film dyed at a given pH and pH 3, respectively. All the cationic groups on the grafted films were fully dissociated at pH 3. As can be seen, D_i/D_∞ of polyDMAEMA grafted films (B) is almost unity below pH 5 and decreases with the increasing pH, reaching zero at pH 10. On the contrary, the D_i/D_∞ value of the films with the introduced quaternary amines (C or D) does not reach zero even at pH 12. D_i/D_∞ of the polyDMAEMA-R₃Br grafted film (D) gradually decreases at pH between 5 and 11, whereas that of the polyDMAEMA grafted film after quaternization (C) steeply decreases in this pH region. It follows that the acidic dye binds to the total amines (tertiary and quaternary) at pH 3 while the dye can bind to only the quaternary amines at pH 10. However, the D_i/D_∞ value at pH 10 is not proportional to the extent of quaternization because of the reduced dissociation at pH 10, as can be seen from the result of D.

DISCUSSION

As demonstrated above, both the two-step and the one-step methods introduce quaternary amines onto the PET film. The methods have both advantages and disadvantages. The two-step quaternization can introduce much more quaternary amines onto the film surface than the one-step, but both tertiary and quaternary amines are present-mixed when the film

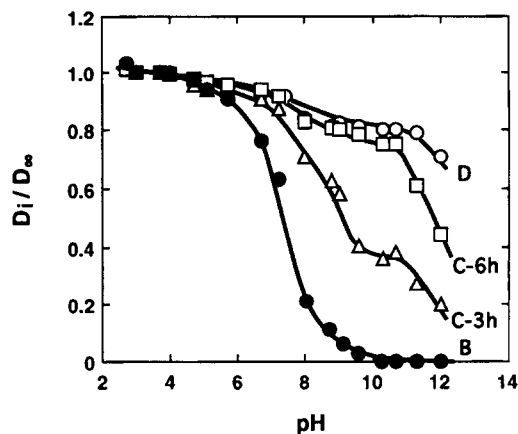


Figure 9 Effect of pH on the adsorption of an anionic dye (Acid Orange 7) at 50°C for 30 min onto grafted PET films carrying introduced tertiary and quaternary amines. (●); B (tertiary amine: graft-polymerized at 1 wt % monomer conc. and 27°C for 1.5 h), (Δ and □); C (R₃Br at 50°C for 3 and 6 h, respectively), and (○); D (quaternary amine: graft-polymerized at 10 wt % monomer conc. and 40°C for 3 h).

is quaternized by the two-step method, as shown in Figure 2. Probably, $R_n\text{Br}$ molecules do not access the polyDMAEMA graft chains that are buried in the PET matrix. Figure 2 suggests that $R_3\text{Br}$ could not access 10% of the graft chains. As larger molecules seem to be less accessible to the graft chains, the decrease in percent quaternization with the increasing carbon number of $R_n\text{Br}$ shown in Figure 3 can be explained in terms of the molecular size of $R_n\text{Br}$. The relatively low graft densities observed for the graft polymerization of DMAEMA- $R_n\text{Br}$ may be also explained in terms of the size of the monomer molecules. In addition, low reactivity and poor compatibility of the quaternary amine monomers with PET might be responsible for the low graft density of these monomers. The dependence of the graft density on the carbon number of $R_n\text{Br}$ found in Figure 6 is not easy to understand. The decreased graft density with the larger carbon number observed for graft polymerization at 20°C may be explained by the same reason as for the result shown in Figure 3. On the other hand, the peculiar dependence of the graft density on the carbon number at 40°C seems to be related to the solubility of the DMAEMA- $R_n\text{Br}$ monomers and polymers in the reaction mixture. In this connection, it should be noted that the DMAEMA- $R_8\text{Br}$ homopolymer was insoluble in water and soluble in acetone at room temperature, in contrast to other homopolymers.

An interesting finding in this study is the good agreement of the carbon number of alkyl chains estimated from the XPS spectra with the theoretical. This indicates that XPS is a very effective means to characterize the film surface carrying tertiary and quaternary amines. The large deviation found for $R_{16}\text{Br}$ may be due to a very low extent of quaternization, because it would make [Br 3_p] in the graft chain very low and obscure, resulting in higher [C1s] than the theoretical.

Finally it should be pointed out that, as Figures 8 and 9 have revealed, the film surface carrying quaternary amine graft chains behaves in aqueous medium quite different from that carrying tertiary amine chains in the high pH region. This is not surprising because tertiary amines have lower pK values than quaternary amines. Therefore, it is highly recommended to use a polymer surface having quaternary amine graft chains when we study the behavior of cationized polymer surface in aqueous media over a wide pH range especially at pH higher than 7. Cellulose films treated with low-molecular-weight cationized groups and chitosan film exhibited almost zero zeta potentials at pH 7.¹⁹

CONCLUSIONS

Quaternary amines could be introduced onto the PET film surface by two different methods using UV-induced graft polymerization; the one involves two-step reactions consisting of graft polymerization of DMAEMA onto the PET film and the subsequent quaternization of the tertiary N,N' -dimethylamino groups of grafted chains using $R_n\text{Br}$, while the other is direct graft polymerization of DMAEMA having pendant quaternary amines onto the PET film. The alkyl bromides used for quaternization of the monomers and graft chains include n -propyl, n -butyl, n -octyl, n -lauryl, and n -cetyl bromide. The evidence for introduction of quaternary amines onto the PET film surface was provided by zeta-potential and XPS spectrum measurements. The two-step method could quaternize 90% of the pendant N,N' -dimethylamino groups of graft chains when $R_3\text{Br}$ was used. The extent of quaternization decreased with the increasing carbon number of alkyl bromide. The direct one-step method gave a graft amine density of 8 nmol/cm², when the monomer quaternized with $R_3\text{Br}$ was used for the graft polymerization in the presence of $1 \times 10^{-3} M$ sodium metaperiodate. When the PET film was subjected to graft polymerization of 10 wt % quaternary amine monomer at 40°C for 4 h, the graft density increased with an increase in the carbon number of the alkyl bromide. The carbon number of alkyl chains in the quaternary amines estimated from XPS spectra was in good agreement with that of $R_n\text{Br}$ used for quaternization except for $R_{16}\text{Br}$.

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