Synthesis and Application of Long-Chain Alkyl Quaternary Ammonium-Functionalized Hyperbranched Polyester

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ABSTRACT: A novel kind of macromolecule, long-chain alkyl quaternary ammonium functionalized hyperbranched polyester (QHPE), was synthesized by the reaction of hyperbranched polyester Boltorn H30 (H30) and 2,3-epoxypropyl alkyl dimethyl ammonium chloride under alkaline conditions in dimethylformamide. After modification, the hydroxyl terminal group of H30 was converted into an ammonium functional group. A series of products was obtained with different lengths of an alkyl chain (C8, C12, C16, and C18) in the ammonium functional group. All of the products were characterized by Fourier transform infrared and NMR spectroscopy. The application of QHPEs as accelerators for the alkaline hydrolysis of poly(ethylene terephthalate) (PET) fabric was studied. The influences of the structure of QHPEs and hydrolysis conditions, such as alkaline concentration, hydrolysis time, and temperature, on the weight loss of PET fabrics were investigated. The results indicated that QHPE was a novel, efficient accelerator for the alkaline hydrolysis of PET fabrics. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2927–2935, 2011

Key words: hyperbranched; quaternary ammonium salt; synthesis; alkaline hydrolysis; PET fabric; accelerator

INTRODUCTION

Hyperbranched polymers (HBPs) are novel, highly branched macromolecules with a three-dimensional structure, low viscosity, low interchain entanglement, and several functional terminal groups. Flory[1] developed the concept of highly branched polymers in the early 1950s, and Kim and Webster[2,3] synthesized the first soluble hyperbranched polyphenylene in 1988. Since then, HBPs have gained great interest because of their easy synthesis and greater potential application compared with dendrimers.[4,5] Some HBPs are already commercially available.[6] It has been shown that HBPs have some different properties from conventional linear polymers because of their globular structures and inner cavities.[1–5]

Unlike conventional linear polymers, terminal groups in HBPs play an important role in the properties of HBPs because of their great number.[4] It is possible to introduce other functional groups with specific requirements by modification of the terminal groups. The functionalization of HBPs has attracted increasing interest in various applications, such as coatings, additives, drug and gene delivery, nanotechnology, and supramolecular science. The alkylation and quaternization of HBPs have been reported.[7–9] Recently, HBPs have been used in textile fields, such as dyeing auxiliaries, antibacterial agents, pigment dispersants, and multifunctional finishing agents.[10–19]

Alkaline hydrolysis is an important method for modifying the chemical and physical properties of poly(ethylene terephthalate) (PET) fabrics. It improves the handling, wettability, resistance to abrasion damage, and soil-resistant properties of fabrics.[20] It was reported that accelerators have always been used to improve the effect of alkaline hydrolysis.[21] However, most accelerators for the alkaline hydrolysis of PET fabrics are low-molecular cationic compounds. The use of polymeric cationic accelerators has been studied to some extent, and it has been shown that polymeric accelerators have a better catalytic efficiency than small molecules because of their stronger capacity for forming hydrophobic interactions with the fiber.[22]

In this study, we synthesized a series of long-chain alkyl quaternary ammonium functionalized

hyperbranched polyesters (QHPEs) Boltorn H30 (H30) as the polycationic accelerator for the alkaline hydrolysis of PET fabrics to impart silklike handling. The effects of the accelerator concentration, NaOH concentration, and hydrolysis time and temperature on the weight loss of the PET fabrics were studied.

EXPERIMENTAL

Materials

The hyperbranched aliphatic polyester H30 was kindly supplied by Perstorp Specialty Chemicals AB (Perstorp, Sweden). The weight-average molecular weight of H30 was 3500 g/mol with a polydispersity (weight-average molecular weight/number-average molecular weight) of 1.5. According to the producer, H30 has an average of 32 hydroxyl terminal groups with a hydroxyl number of 480–510 mg of KOH/g.[23]

The dimethyl alkylamines (C8, C10, C12, and C16) were commercial products (98%) from Feixiang Chemicals Co., Ltd. (Jiangsu, China) Hexadecyl trimethyl ammonium bromide (HTAB), epichlorohydrin, N,N-dimethylformamide (DMF), ethyl acetate, and sodium hydroxide were analytical-reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) All of the chemicals were used without further purification. Polyester fabrics (76 dtex, 240 T) were supplied by Shanghai Hualun Printing & Dyeing Co., Ltd. (Shanghai, China) Fourier transform infrared (FTIR) spectra were recorded on a Varian 600-IR spectrometer (Varian, USA) with potassium bromide disks between 4000 and 500 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400-MHz NMR spectrometer (100 MHz, Bruker, Switzerland) in hexadeuterated dimethyl sulfoxide with TMS as an internal standard. The surface morphologies of the PET fabrics before and after alkaline hydrolysis were examined with scanning electron microscopy (SEM; JSM-5600, JEOL, Japan) with an accelerating voltage of 10 kV.

Synthesis of the long-chain alkyl QHPE

The ideal molecular formula of H30 and the synthesis of QHPE are illustrated in Scheme 1. The synthesis of QHPE was carried out in two steps. In the first step, long-chain alkyl epoxypropyl dimethyl ammonium chloride (EPA) was obtained by the reaction between epichlorohydrin and long-chain alkyl dimethyl amines. In the second step, H30 was modified by EPA to transfer the hydroxyl terminals to the ammonium functional groups.

A typical example of epoxylpropyl dimethyl hexadecyl ammonium chloride was synthesized as follows: N,N-dimethylhexadecylamine (100 mmol) was added slowly over a period of 30 min to epichlorohy-
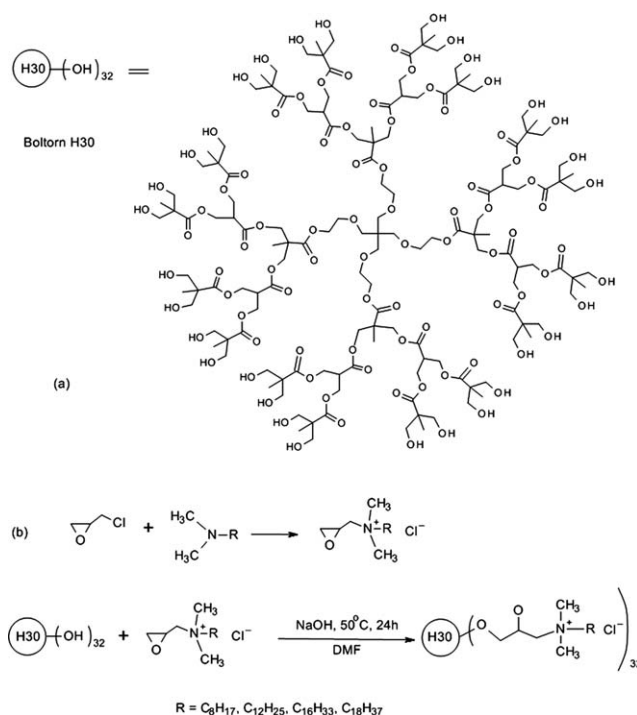
Scheme 1 (a) Ideal molecular formula of H30. (b) Synthesis of QHPE (H30C8N, H30C12N, H30C16N, and H30C18N).

drin (429 mmol), which was also used as a solvent and maintained at room temperature for 10 h. After the completion of reaction, the resulting product was precipitated in ethyl ether and dried in a vacuum desiccator. The epoxylpropyl dimethyl alkylammonium chlorides obtained with different lengths of alkyl chain (R=C$_8$H$_{17}$, C$_{12}$H$_{25}$, C$_{16}$H$_{33}$, and C$_{18}$H$_{37}$) in the ammonium functional group were named EPA8, EPA12, EPA16, and EPA18, respectively.

H30 was modified by EPA to obtain its ammonium functionalities. A typical example preparation procedure for epoxylpropyl dimethyl hexadecyl ammonium substituted H30 was shown as follows. H30 (10.5 g, 80 mmol of terminal hydroxyl groups) was dissolved in DMF and added to a three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser with a drying tube. Solid NaOH (1.92 g) was then added and stirred for 10 min. After that, EPA16 (34.75 g) solution in DMF was added dropwise successively into this reaction vessel under stirring at 50°C for 24 h. After the mixture was cooled to room temperature, NaOH was removed by filtration. The solvent was removed on a rotary evaporator under reduced pressure. The crude product was further purified by exhaustive dialysis against deionized water with an osmosis membrane (molecular weight cutoff = 1000 g/mol, Shanghai Greenbird Science & Technology Co., Shanghai, China) to remove unreacted small molecules. Finally, the residual was stored in a vacuum

desiccator for 1 day and stored in the desiccator because of its high moisture sensitivity. A series of products was obtained with different lengths of the alkyl chain (R=C_8H_{17}, $C_{12}H_{25}$, $C_{16}H_{33}$, and $C_{18}H_{37}$) in the ammonium functional group for different times; these were named H30C8N, H30C12N, H30C16N, and H30C18N, respectively.

Critical micelle concentration (cmc)

The conductivity was measured at 298 ± 0.2 K with a conductivity meter (model DDS-11A, Leici, Shanghai, China). All of the sample solutions were prepared with double-distilled water. For every QHPE compound, the conductivity was determined with 8–10 aqueous solutions at different concentrations. After that, all of the data were plotted to illustrate the relationship between the conductivity and the QHPE concentration. All of the points were located along two intersecting straight lines. The intersection point was taken as cmc.[24]

Alkaline hydrolysis of the PET fabric

Alkaline hydrolysis of PET fabric was carried out with a liquor ratio of 1 : 25. The PET fabric sample was immersed in an Erlenmeyer flask with the required amount of NaOH and accelerator and treated for certain time at the required temperature. The bath temperature was increased at a rate of 2.2°C/min until the required temperature was reached. After treatment, the PET fabric was removed from the bath and rinsed thoroughly with hot water, neutralized with a solution of 1% hydrochloric acid, and then rinsed and dried.

The weight loss of the treated polyester fabric was calculated according to the following equation:

$$\text{Weight loss } (\%) = \frac{(W_1 - W_2)}{W_1} \times 100\%$$

where W_1 and W_2 are the weights of the samples before and after alkaline hydrolysis, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization of QHPE

QHPE H30 was prepared by the etherification of H30 with EPA in the presence of an alkaline catalyst for different times (Scheme 1). Under alkaline conditions, the terminal hydroxyl groups of H30 first became alcoholate anions and then attacked the epoxy group of EPA to form an ether bond. However, the epoxy group also hydrolyzed in the alkaline solutions; this decreased the degree of quaternization of QHPE.
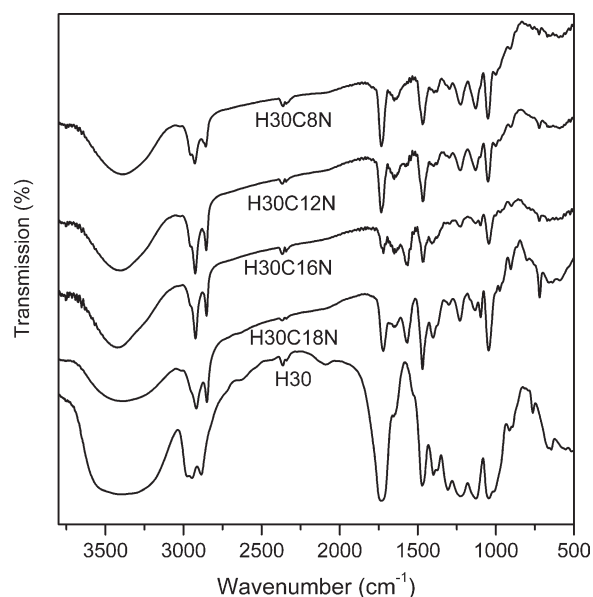

Figure 1 FTIR spectra of H30 and QHPEs.

The reaction of H30 was conducted with NaOH, triethylamine, and pyridine as the alkaline catalyst in DMF, respectively. The solution turned from colorless to light yellow and finally became dark brown under organic alkaline catalysts. The color change may have been due to the decomposition of catalyst during the reaction process. Moreover, the change of the cationization reagent EPA was not detected by TLC testing during the reaction. This could have been to the weak alkalinity of those organic catalysts. Although aqueous sodium hydroxide has strong alkalinity for the etherification reaction, it would have increased the hydrolysis of the ester bond of H30 under heating for long time. On the basis of these considerations, we chose solid sodium hydroxide as the catalyst.

All compounds were characterized by FTIR and NMR spectroscopy. The FTIR spectra of H30 and QHPE (H30C8N, H30C12N, H30C16N, and H30C18N) are presented in Figure 1. The FTIR spectra of QHPE exhibited a similar absorption, as expected because of their similar chemical structure. The FTIR spectra of H30 and QHPE both showed strong bands at 3200 to 3600 cm^{-1}, which were assigned to ─OH stretching vibrations. The bands around 2800–3000 cm^{-1} were attributed to the symmetric and asymmetric stretching vibration of ─CH_2 and ─CH_3 groups. The band at 1730 cm^{-1} was assigned to C=O stretching vibrations of H30, and a small shift was found in QHPEs. The bands at 1470 and 1400 cm^{-1} were attributed to ─CH_2 and ─CH_3 bending, respectively. A weak absorbance at 720 cm^{-1} showed that long alkyl groups were added to H30; this was also confirmed by the ratio of relative intensity $R = I_{1470}/I_{1400}$ between the adsorption peak at 1470 cm^{-1} (I_{1470}) and that at 1400 cm^{-1} (I_{1400}) is greater in QHPEs than in H30. The presence of an
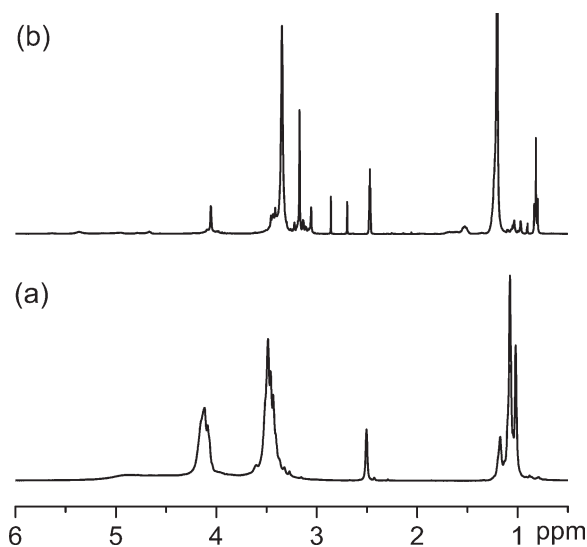
Figure 2 ¹H-NMR spectra of (a) H30 and (b) H30C16N.

additional band at 1100 cm^{-1} assigned to the stretching of C—O—C, which was formed by the reaction between the H30 hydroxyl group and the EPA epoxy group, was supporting evidence for the successful reaction between H30 and EPA. These differences of the spectra in H30 and QHPE confirmed the formation of H30 ammonium functionalities.

All QHPE compounds were also characterized by ¹H-NMR and ¹³C-NMR spectra. The structure was illustrated by the example of H30C16N. Because of the branched polymer structure, it was difficult to attribute all of the peaks but there were still some unique ones. The ¹H-NMR spectra of H30 and H30C16N are shown in Figure 2. The strong additional peak at 3.18 ppm, which was assigned to the methyl and methylene protons of the quaternary ammonium group of H30C16N (—CH$_2$—N$^+$—CH$_3$), indicated the combination of H30 and EPA16. Figure 3 shows resonances at 175 ppm, which could have been due to the carbonyl carbon of both H30 and H30C16N. The resonances associated with —CH$_2$ and —CH$_3$ in H30 appeared in the region between 15 and 55 ppm. However, Figure 3(b) shows some additional peaks, which may have been due to —CH$_2$ and —CH$_3$ in the long-chain moiety of H30C16N in this region from 15 to 55 ppm. The results indicate that the structure of H30 changed and that some additional —CH$_2$ and —CH$_3$ groups were added to H30.

In addition, H30 was insoluble in polar solvents, such as water. However, all of the QHPEs could dissolve in water. The changes in the solubility between H30 and QHPEs also indicated that H30 was successfully modified. The solubility of the QHPEs decreased with increasing length of the alkyl groups in the quaternary ammonium salt part. It was noticeable that all of the QHPEs had a higher solubility in water than HTAB.

cmc

The foaming properties of QHPE indicated surface activity. The cmc values of the modified hyperbranched polyester were measured through the conductivity of the QHPE solution. Figure 4 illustrates the dependence of the conductivity with concentration for the investigated QHPE. Two regression lines with different slopes were observed, and the intersection was taken as cmc. An expected, a decrease in the cmc values was observed with increasing length of the alkyl chain modified on H30.

Alkaline hydrolysis of PET fabric with QHPE as an accelerator

The alkaline hydrolysis behavior of PET fabric with different types of QHPE accelerators (H30C8N, H30C12N, H30C16N, or H30C18N) was investigated. The effect of HTAB on the alkaline hydrolysis of PET was also studied as a control.

Effects of the structure and concentration of the accelerator QHPE

In the process of the alkaline hydrolysis of PET fabrics, the hydrolysis rate was related to the concentration of OH$^-$ and the electron-deficient carbonyl carbon of the fiber.[20] The hydrophobic nature of the PET fibers made it difficult to attach hydroxyl ions in the solution, even at high concentration. The effect of the quaternary ammonium surfactant can be explained as follows. On the one hand, the surfactant decreased the surface tension and was, therefore, easily absorbable onto the fiber; on the other hand, the electrostatic attractions between the quaternary ammonium surfactant cations and the hydroxyl ions
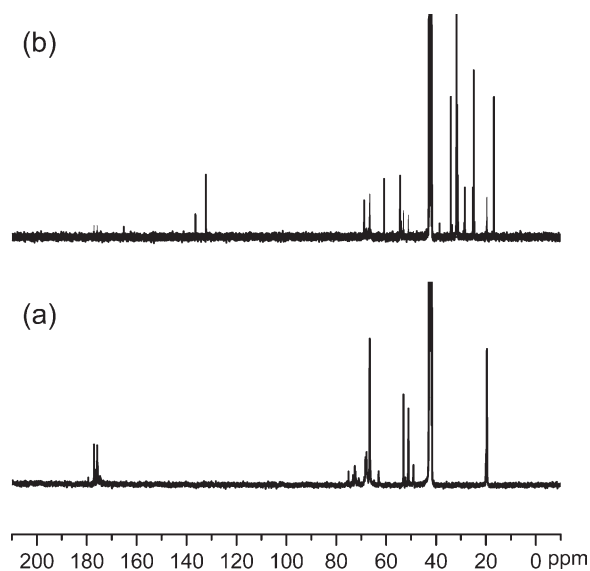

Figure 3 ¹³C-NMR spectra of (a) H30 and (b) H30C16N.
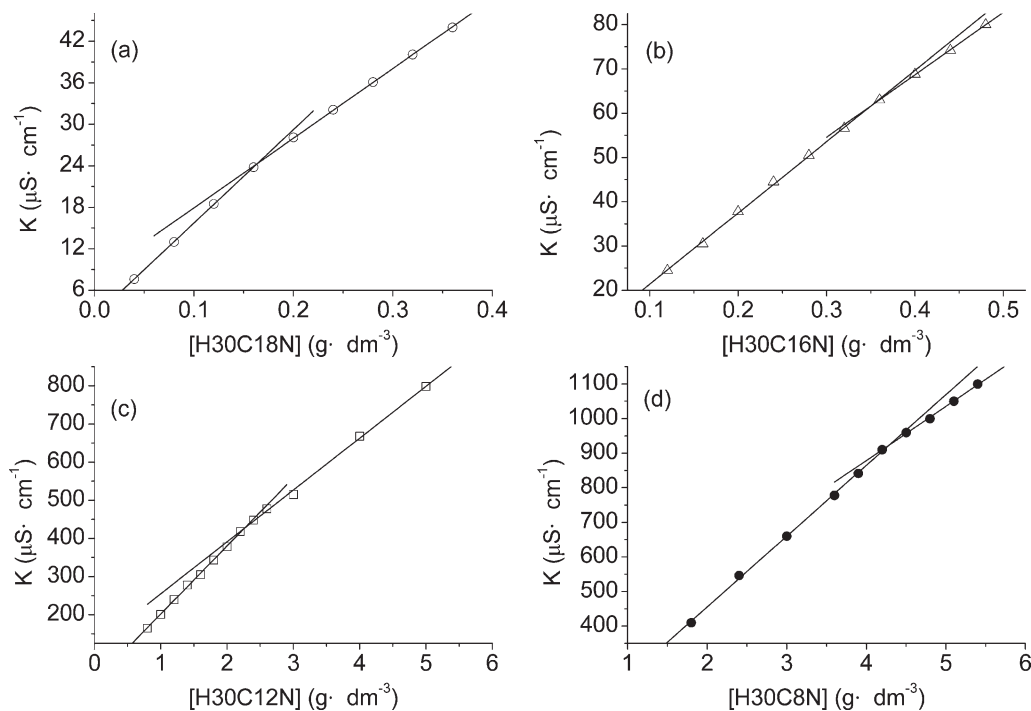
Figure 4 Relationship between the conductivity and concentration of QHPEs.

also attracted OH⁻ to the fiber and accelerated the hydrolysis of the PET fibers.

Figure 5 presents the effects of the structure and concentration of QHPEs on the weight loss of the PET fabrics. The incorporation of QHPEs in the alkaline bath greatly accelerated the alkaline hydrolysis reaction, even at a low concentration. The weight loss of the PET fabrics increased first, apparently with increased accelerator concentration, and then slowly, eventually approaching the maximum for all accelerators except H30C8N. The accelerator H30C8N with eight carbon chains had a limited catalytic effect with maximum of 5.34% weight loss of PET at 1.6 g/dm³. H30C12N showed a rapid increase in the first stage, below 1.6 g/dm³, and then increased slowly until equilibrium was obtained at 3.2 g/dm³ with a similar maximum weight loss as that of H30C16N, around 30%. The other three accelerators (H30C16N, H30C18N, and HTAB) greatly increased the hydrolysis rate of the PET fabrics, even at a low concentrations. The equilibrium concentrations were different for these accelerators and ranged from 0.16 to 0.32 g/dm³ at the maximum weight loss. Further addition of accelerators above the equilibrium concentrations did not show a significant effect on the weight loss. This could have been due to the fact that extra accelerators formed micelles in the solution and lost their catalytic capability.

The results indicate that the length of the alkyl chain of the accelerators influenced their catalytic performance. Accelerators with longer lengths of the alkyl chain showed higher hydrolysis rates in the growth part of the rate curves, and lower concentrations were required to obtain equilibrium. With increasing length of the alkyl chain, the reduction of the surface tension became greater, the accelerators were more easily absorbed onto the fiber surface, and the hydrolysis reaction occurred more rapidly. The equilibrium concentration of the accelerator was on the order of H30C18N < H30C16N < H30C12N. Compared with the cmc values mentioned previously, we concluded that the maximum weight loss was also obtained at the cmc of the accelerator.[25]
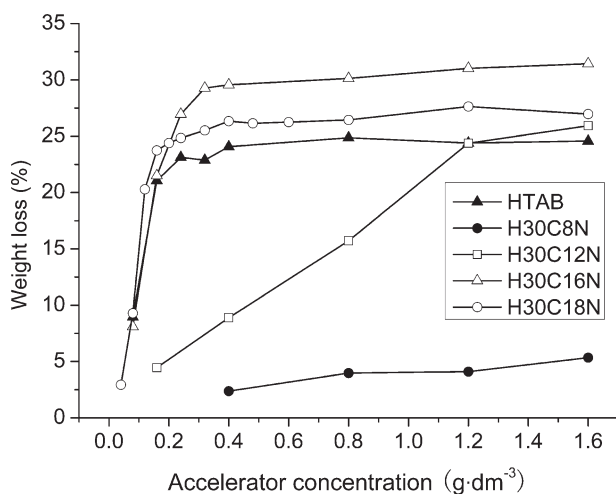

Figure 5 Effects of the structure and concentration of the accelerators on the weight loss of the PET fabric with 8 g/dm³ NaOH at 98°C for 60 min.

H30C16N was more effective than HTAB as an accelerator. There were two possible reasons. First, the synergistic effect of multiple quaternary ammonium groups in the polycationic H30C16N showed greater electrostatic attractions to OH^- in solution than HTAB. Second, compared with HTAB, H30C16N had a stronger affinity with the PET fabrics because of its high film-forming properties and weaker interaction with combined OH^- on the surface of fiber because of its bigger molecular volume.

Effect of the NaOH concentration

Figure 6 illustrates the effect of the NaOH concentration on the weight loss of the PET fabrics. At a constant temperature and time, the weight loss increased with increasing concentration of NaOH. With more NaOH, hydroxyl ions were more easily attached at various places of the long chain; this resulted in an increased frequency attack of the electron-deficient carbonyl carbon in the PET fabrics. Apparently, the relationship between the weight loss and NaOH concentration was linear whether or not accelerator was present.

The addition of QHPEs improved the utilization rate of NaOH for the hydrolysis of the PET fabrics. A weight loss of 7.00% was obtained at 20 g/dm³ NaOH without the accelerator. Under the same conditions, the weight losses obtained were 14.49, 48.11, and 39.47% for products treated with 0.16 g/dm³ H30C12N, H30C16N, and H30C18N, respectively. In addition, the weight losses obtained with 4 g/dm³ NaOH and 0.16 g/dm³ H30C16N or H30C18N were much higher those obtained without accelerator at 20 g/dm³ NaOH. Therefore, the accelerators played a very important role in the alkaline hydrolysis of the PET fabrics. A large amount of sodium hydrox-
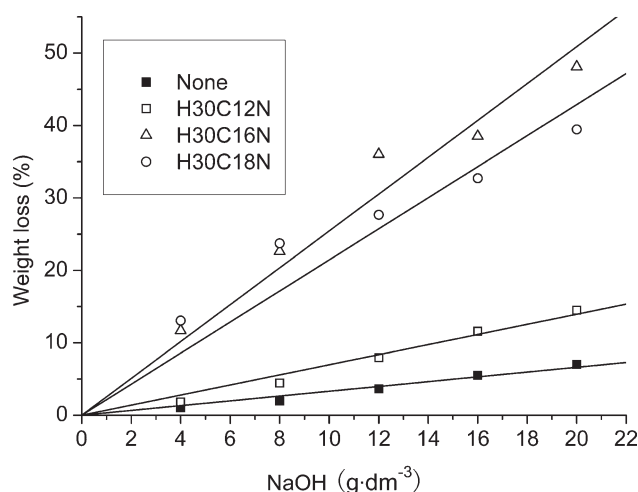
Figure 6 Effect of the NaOH concentration on the weight loss of the PET fabric with 0.16 g/dm³ accelerators at 98°C for 60 min.

TABLE I
pH Values of the QHPEs (H30C12N, H30C16N, and H30C18N) in NaOH Solution (8 g/dm³) for Different Times

Time (min)	H30C12N (g/dm³)		H30C16N (g/dm³)		H30C18N (g/dm³)	
	0.16	40	0.16	40	0.16	40
0	13.14	13.07	13.14	13.09	13.11	13.09
15	13.11	13.06	13.11	13.08	13.13	13.06
30	13.12	13.07	13.13	13.08	13.12	13.08
45	13.12	13.06	13.12	13.08	13.11	13.07
60	13.11	13.06	13.12	13.06	13.08	13.06

ide could be saved by the addition of an appropriate amount of accelerator.

The stability of QHPEs (H30C12N, H30C16N, and H30C18N) in NaOH solution was studied to make sure that all of the accelerators were stable during the process of alkaline hydrolysis. The pH changes were performed both at 0.16 and 40 g/dm³ QHPEs in 8 g/dm³ NaOH solution, as presented in Table I. No obvious pH changes were found, even at 40 g/dm³ QHPEs. This indicated that QHPEs were stable during the alkaline hydrolysis process.

Effect of the hydrolysis time

Figure 7 shows the relationship between the weight loss and hydrolysis time at 351, 361, and 371 K in the absence and presence of accelerator (H30C12N, H30C16N, and H30C18N). In all cases, satisfactory linearity was obtained,[26,27] and the effective hydrolysis rate constant was also calculated. The relationship between the weight loss and time can be written as follows:[27]

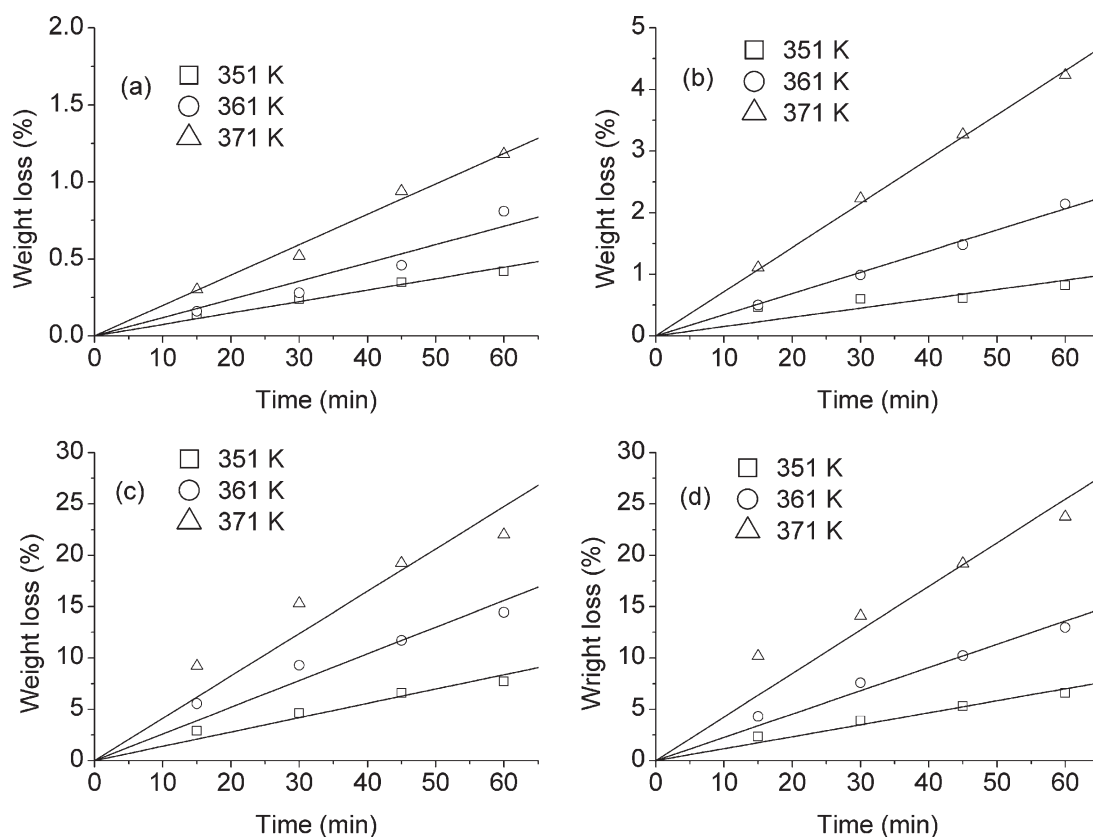$$\text{Weight loss } (\%) = kt$$

where k is a constant dependent on temperature and the concentration of NaOH and accelerator and t is the hydrolysis time.

k was obtained from the slope of the lines, as shown in Table II. The results indicate that a higher rate of alkaline hydrolysis was attained in the presence of accelerator (H30C12N, H30C16N, or H30C18N) than that of hydrolysis without the accelerator. The temperature dependence of the rate k can be described in terms of the activation energy (E_a) according to the Arrhenius equation:

$$k = B \cdot \exp(-E_a/RT)$$

where B is the pre-exponential factor, T is the thermodynamic temperature, and R is the molar gas constant.

The plot of $\ln k$ versus $1/T$ is linear with a slope equal to $-E_a/R$, and the intercept is equal to $\ln B$.

Figure 7 Relationship between the weight loss and time in the absence and presence of 0.16 g/dm³ accelerators with 8 g/dm³ NaOH: (a) absence, (b) H30C12N, (c) H30C16N, and (d) H30C18N.

The presence of accelerator QHPEs changed the values of both E_a and B.[28] Higher E_a and B values were obtained in the presence of QHPEs than without the accelerator. The higher the E_a value was, the lower the hydrolysis rate was at a low temperature. In contrast, the higher B was, the higher the hydrolysis rate was. QHPEs with different lengths of the alkyl chain had different E_a and B values. With increasing length of the alkyl chain, E_a decreased at first from H30C12N to H30C16N and then increased from H30C16N to H30C18N. The same trend was found for B.

Effect of the hydrolysis temperature

Figures 8 and 9 present the effect of the temperature on the weight loss of the PET fabric. The increase in the temperature caused an increase in the weight loss

TABLE II
Linear Relationship Between Weight Loss and Hydrolysis Time at Three Different
Temperatures in the Absence and Presence of Accelerators

| Sample	Temperature (K)	k $(R^2)^a$	E_a (kJ/mol)	$\ln B$ (s^{-1})	R^2
Absence	351	0.0074 (0.9965)			
	361	0.0119 (0.9706)	52.98	13.24	0.9995
	371	0.0197 (0.9923)			
H30C12N	351	0.0151 (0.9451)			
	361	0.0344 (0.9971)	84.43	24.74	0.9999
	371	0.0718 (0.9994)			
H30C16N	351	0.1394 (0.9943)			
	361	0.2600 (0.9956)	58.78	18.19	0.9976
	371	0.4124 (0.9847)			
H30C18N	351	0.1165 (0.9989)			
	361	0.2267 (0.9988)	69.96	21.82	1.0000
	371	0.4242 (0.9988)			

ª The number in parentheses is the corresponding R^2 of the linear fitting in Figure 7.
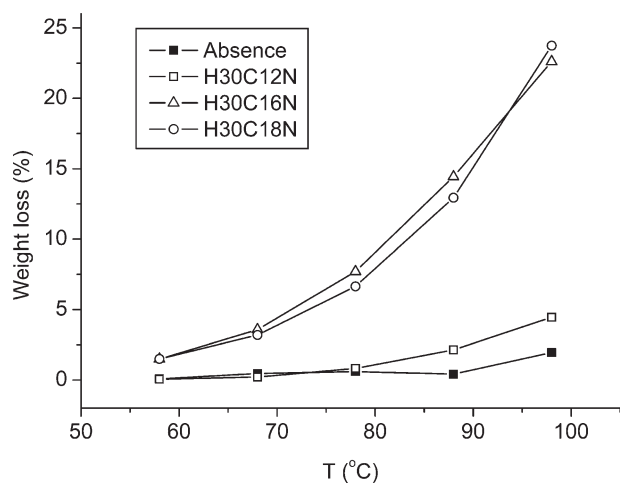
Figure 8 Effect of the temperature on the weight loss of the PET fabric in the absence and presence of 0.16 g/dm^3 accelerators with 8 g/dm^3 NaOH for 60 min.
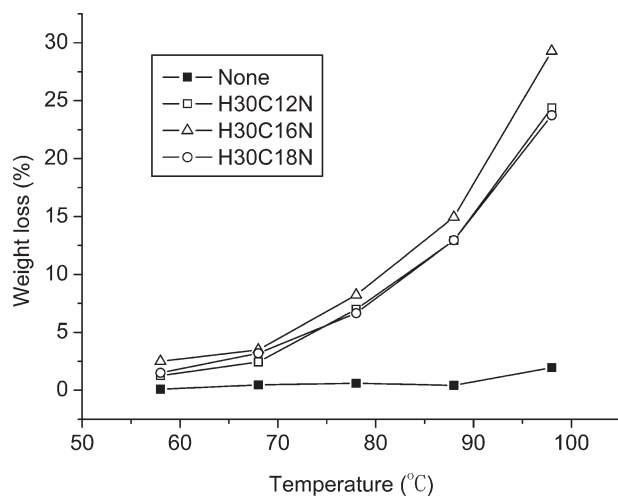
Figure 9 Effect of the temperature on the weight loss of the PET fabric in the absence and presence of accelerators (1.6 g/dm^3 H30C12N, 0.32 g/dm^3 H30C16N, and 0.16 g/dm^3 H30C18N) with 8 g/dm^3 NaOH for 60 min.
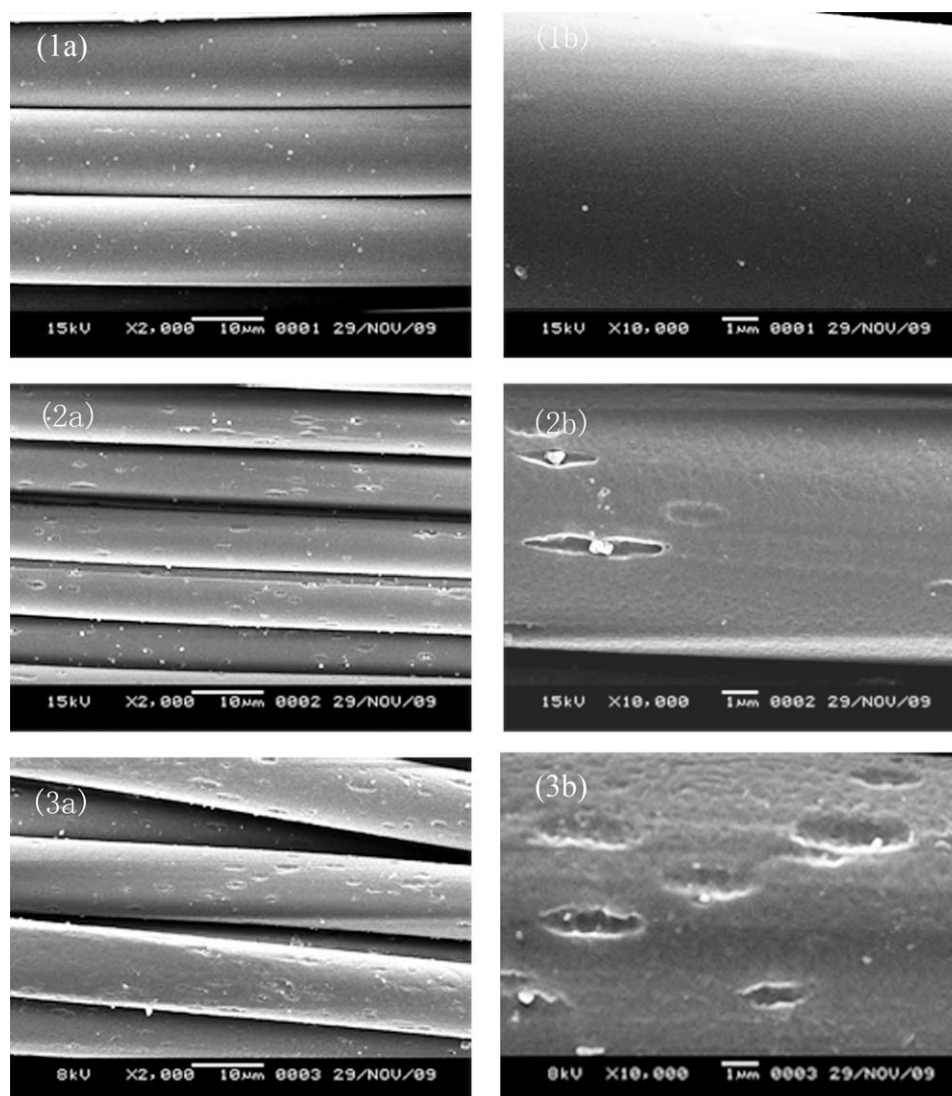
Figure 10 SEM images of the PET fabric treated with 8 g/dm^3 NaOH and 0.16 g/dm^3 H30C16N for different hydrolysis times: (1a,1b) untreated; (2a,2b) 45 min, weight loss = 21.3%; and (3a,3b) 70 min, weight loss = 29.3%.

for all of the reactions. The weight loss at first increased slowly with increased temperature and then increased rapidly when the temperature exceeded the glass-transition temperature of PET ($\sim 80°C$). Furthermore, the influence of the temperature on the weight loss was interrelated to the amount of accelerator used. The alkaline hydrolysis of the PET fabrics was a double-diffusion reaction process. That is, the reactant OH^- diffused from the solution to the fiber surface, amorphous region, and edge of the crystalline region, whereas the hydrolysis product diffused from fiber to the solution. At a low temperature, the fiber molecules were frozen in place in the amorphous regions, and the hydrolysis rate was very slow. At temperatures above the glass-transition temperature, the segmental mobility of the polymer chains increased, so the rate of alkaline hydrolysis was enhanced.

SEM

The SEM images of the PET fabrics with different weight losses presented in Figure 10 were similar to those of other studies.[25,27,29] The results indicate that the addition of accelerator did not change the basic mechanism of the hydrolysis reaction of the PET fabrics in alkaline solution.[25] The surface of the untreated fiber was fairly smooth. The surface of the PET fiber was obviously etched and roughened after alkaline hydrolysis; this resulted in the formation of the pitlike structure on the surface of the PET fibers. Moreover, hydrolysis was carried out uniformly throughout the whole surface of the fiber, and the fabric structure gradually became loose. With increasing hydrolysis time, the roughness of the surface increased. The depth and frequency of pits on the surface also increased.

CONCLUSIONS

A series of QHPEs was synthesized. FTIR and NMR spectra confirmed that the hydroxyl terminal group of H30 was converted into an ammonium functional group. The synthesized QHPE was demonstrated as a kind of novel, efficient accelerator for the alkaline hydrolysis of PET fabrics. QHPE exhibited a greater effectiveness for the alkaline hydrolysis of the PET fabrics compared to a conventional ammonium compound. Because QHPE was polycationic with multiple quaternary ammonium cations, it may have had greater electrostatic attractions to OH^- and indicated an increase in weight loss because of additional hydroxyl anion.

QHPE showed a stronger affinity with PET fabrics but weaker interactions with combined OH^- on the surface of the fabric because of its bigger molecular volume, so it was easier for nucleophile $-OH$ to attack the electron-deficient carbon of the fabric.

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