Grafting of Methyl Methacrylate onto Sodium Alginate Initiated by Potassium Ditelluratoargentate(III)

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ABSTRACT: Sodium alginate (SA) was graft-copolymerized with methyl methacrylate in an alkali aqueous solution with potassium ditelluratoargentate(III) (DTA) as the initiator. Graft copolymers with both a high grafting efficiency (>90%) and a high percentage of grafting were obtained, which indicated that the DTA–SA redox pair was an efficient initiator for this grafting. The grafting parameters, including total conversion, grafting efficiency, and percentage grafting, were evaluated comparatively. The dependence of these parameters on temperature and time, monomer concentration, initiator concentration, and SA backbone concentration was also investigated. The overall activation energy of this grafting was calculated as 37.50 kJ/mol. Proof of grafting was obtained from gravimetric analysis and IR spectra. A tentative mechanism involving a two-step, single-electron-transfer process of DTA is proposed to explain the generation of radicals and the initiation of grafting. Some basic properties of the grafted copolymer were studied by instrumental analyses, including thermogravimetry, X-ray diffraction, and scanning electron microscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1688–1694, 2005

Key words: monomers; graft copolymers; radical polymerization

INTRODUCTION

Algin, or alginate, is a gelatinous substance produced by brown algae and is used in a wide range of food, leather, pharmaceutical, and industrial applications. Because it is one of the few hydrocolloids that are capable of both thickening and gelling water, algin offers many useful properties, including viscosity control, stabilization of suspensions, emulsions and foams, improved freeze–thaw stability, syneresis and boilout control, film formation, rheology control, and more. Algin has many useful properties and is very user-friendly and consumer-friendly because it is renewable, biodegradable, vegetable and not animal in origin, and wholly safe by all known tests.[1] However, it is prone to enzymatic degradation and suffers from limitations in fabrication, which limits its application in some fields, for example, in controlled-release technology.[2]

Grafting is a well-established and powerful method for the development of natural–synthetic polymer hybrid materials. Among chemical initiation methods, redox-initiated grafting offers advantages because in the presence of a redox system, grafting can be carried out under milder conditions and side reactions are at a minimum. So far, the grafting of vinyl monomers onto alginate has been carried out with ceric(IV) ions,[3–7] persulfate,[8] a redox pair of persulfate with urea[9] or thiourea,[10] hydrogen peroxide,[11] a couple of hydrogen peroxide molecules with ferrous,[12] ascorbic acid,[13] and others. With these initiators, ceric(IV) ions were used most extensively because of the higher extent of grafting compared with the others. However, its high price and acid reactant medium limit its application to some extent because alginic acid is insoluble in water.

In our previous studies, potassium diperiodatoargentate(III) (DPA), coupled with various reducing agents, was shown to be an effective initiator in both homopolymerization[14,15] and graft copolymerization.[16–19] A two-step, single-electron-transfer mechanism when DPA reduced was well established as a way to explain the formation of radicals and the initiation. However, now, the use of potassium ditelluratoargentate(III) (DTA) as an oxidizing agent is well known and has been extensively studied in micrometric determinations[20] and in kinetic studies of the oxidations of some organic compounds.[21–23] Commonly, it is believed that the mechanism of oxidation by DTA is a two-electron-transfer process without the production of intermediate radicals. In previous studies, we developed conditions for the homopolymerization of acrylamide[24] and the grafting of methyl acrylate on cellulose[25] with DTA as initiator and confirmed that DTA is an efficient radical initiator.

In this study, methyl methacrylate (MMA) was successfully grafted onto sodium alginate (SA) with DTA,

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which is superior to ceric ions because of the solubility of SA in water and the higher grafting efficiency (GE; >90%). The study further confirmed that the reduction of Ag(III) could proceed through a two-step, single-electron-transfer process under appropriate conditions no matter if periodate or tellurate was used as the complexing agent. In addition, the effect of different factors on the grafting was investigated in detail. The grafted products were characterized with IR spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and X-ray diffraction.

EXPERIMENTAL

Materials

SA, obtained from Damao Chemical Reagent Station (Beijing, China), was washed with acetone to remove any adhering impurities before use and was then dried under reduced pressure. MMA, from Tianjin Xintong Chemical Reagent Station (Tianjin, China), was washed successively with an aqueous sodium hydroxide solution and distilled water and was then dried over anhydrous sodium sulfate and distilled under reduced pressure. The middle fraction was used. The DTA stock solution was synthesized and standardized according to a reported procedure.[26] The other reagents, including KOH, $K_2S_2O_8$, K_2TeO_4, $AgNO_3$, acetone, methanol, and acetic acid, were all analytical grade and were used without any further purification.

Polymerization procedure

In a typical experiment, the graft copolymerization was carried out as follows: a requited amount of SA was dissolved completely in water in a 50-mL stoppered conical flask, which we deaerated sufficiently by sparging with nitrogen, and equilibrated at the required temperature with constant stirring. The required amount of monomer was then added, followed by the addition of DTA aqueous solution, and the total volume of the reaction mixture was made up to 20 mL with distilled water. After the required reaction time, the reactant was cooled and neutralized by aqueous acetic acid solution, and then, it was poured into an excess of methanol to precipitate the crude copolymer. The precipitated product was filtered through a weighted, sintered glass funnel, washed to neutral with methanol, and dried to a constant weight at 80°C under reduced pressure. The homopolymer of methyl methacrylate [poly(methyl methacrylate) (PMMA)] was removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 h. The final copolymer was then dried to a constant weight again.

The grafting parameters, including total conversion (TC), GE, and percentage grafting (PG), were defined and calculated as follows:

$$\text{TC (\%)} = (\text{Total weight of PMMA} / \text{Weight of MMA charged}) \times 100\%$$

$$\text{GE (\%)} = (\text{Weight of PMMA grafted} / \text{Total weight of PMMA}) \times 100\%$$

$$\text{PG (\%)} = (\text{Weight of PMMA grafted} / \text{Weight of backbone}) \times 100\%$$

Measurements

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the pure SA, PMMA, and SA-*g*-PMMA were recorded on an FTS-40 spectrometer (Bio-Rad Co.) with the potassium bromide pellet technique.

Thermal analysis

TGA curves of the ungrafted and grafted SA were carried out on a Shimadzu apparatus (DGC-40 DTA-TG, Reili Analyse Apparatus Corp., Beijing, China) at a heating rate of 10°C/min in a static air atmosphere.

SEM

A scanning electron microscope (1000B-2, Scientific Apparatus Factory of Chinese Academy of Science, Beijing, China) was used to observe the morphologies of SA and SA-*g*-PMMA.

X-ray diffraction

X-ray diffraction of the ungrafted and grafted SA was measured with a Y-4Q X-ray diffraction instrument (Dandong Ray Apparatus Corp., Jilin Province, China). The X-ray diagrams were made with Ni-filtered Cu Kα radiation at 30 kV and 20 mA.

RESULTS AND DISCUSSION

To gain an insight into the reaction, we investigated the effects of synthetic variables, including temperature and time, monomer amount, initiator concentration, and backbone concentration, on the grafting parameters.

Effect of temperature and time

The effect of temperature and time on the grafting of MMA on SA were determined at four different temperatures from 10 to 40°C. As shown in Figures 1 and 2, the curves for TC versus time and PG versus time show a similar trend due to the high and almost unchanged GE (ca. 95%) at all times.

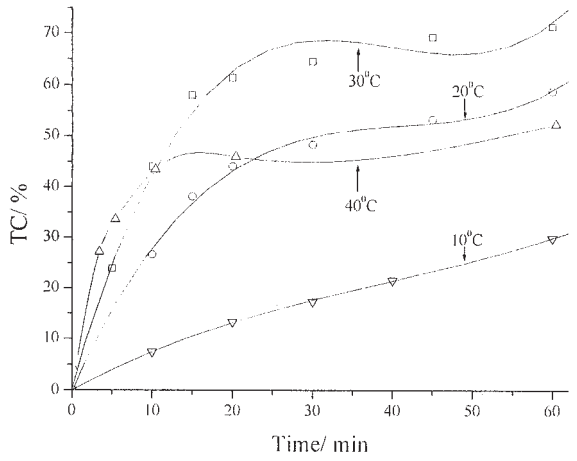

Figure 1 Effect of temperature and time on TC percentage: [DTA] = 0.529×10^{-3} mol/L, volume (MMA) = 1.6 mL, and [SA] = 10 g/L.

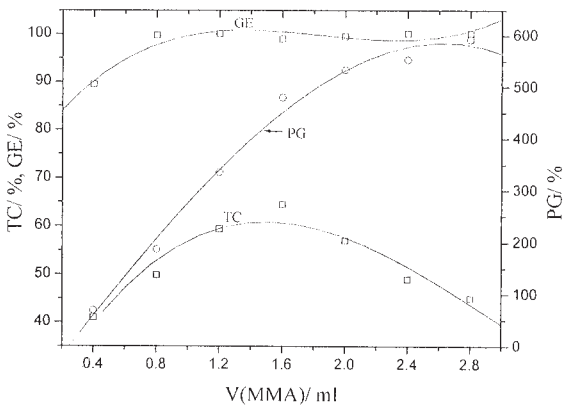

Figure 3 Effect of MMA amount on the grafting parameters: [DTA] = 0.529×10^{-3} mol/L, [SA] = 10 g/L, temperature = 25°C, and reaction time = 30 min.

For a given temperature, except for the reaction at 10°C (at this temperature, the TC and PG increased almost linearly within the range studied), the TC and PG increased steadily with increasing reaction time to a certain value (20 min for the reactions at 20 and 30°C and 10 min for the reaction at 40°C) and then leveled off. The initial increase in TC and PG clearly indicated that both DTA and the grafting sites kept their activity for a period of time. The following trend of leveling off was attributed to the decrease in monomer concentration and initiator concentration and a reduction in the number of active sites on the SA backbone.

In addition, with increasing temperature, as expected, there was an increase in the initial rate of polymerization (R_{pi}) and rate of grafting (R_{gi}). The acceleration in R_{pi} and R_{gi} with increasing temperature was consistent with the general principle of conventional radical polymerization; that is, the increase in temperature enhanced the mobility of the SA, DTA, and monomer molecules, as this increased the chances of encounters among them, and thus, the R_{pi} and R_{gi} accelerated. At the same time, the decline in the viscosity of the reaction system with increasing temperature may have also accounted for this to a certain extent. However, at the latter stage (after 20 min), the magnitude of the TC and PG followed the order 30 > 20 > 40 > 10°C. The tendency a lower TC and PG at a higher temperature (40°C in this study) may have been due to a faster termination rate of the growing chain through oxidation by DTA, which in reverse, accelerated the consumption of the DTA.

To calculate the activation energy of the reaction, the R_{pi} of each temperature was determined from the corresponding curve of TC versus time by the drawing of a tangent. With ln R_{pi} plotted against 1/temperature, the overall activation energy was calculated as 37.50 kJ/mol.

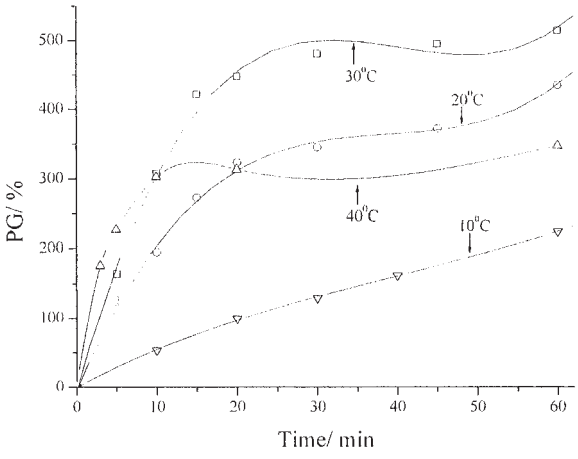

Figure 2 Effect of temperature and time on PG: [DTA] = 0.529×10^{-3} mol/L, volume (MMA) = 1.6 mL, and [SA] = 10 g/L.

Effect of monomer amount

The influence of monomer amount on the grafting of MMA on SA is depicted in Figure 3. In the beginning, TC and PG increased rapidly with increasing monomer amount up to 1.6 mL, and thereafter, PG increased gradually, whereas TC declined. At the same time, GE exhibited a tendency to increase first up to 1.2 mL and then remain almost unchanged. The initial increasing trend of all of the grafting parameters may have been associated with the higher availability of monomer molecules to the SA macroradicals. The following decreasing trend of TC could have been due to the too large ratio of MMA to the grafting sites; that is, the DTA was relative deficient to the MMA at a too high monomer amount, so although the absolute amount of grafted polymer increased, which was evident by the increase in PG at all times relative to the fast increase in MMA, TC decreased.

Effect of DTA concentration

As shown in Figure 4, when the DTA concentration was varied (0.44–1.23 $\times$ 10^{-3} mol/L), TC and PG increased significantly at first, passed through a maximum, and then decreased. The initial increasing trend may have been a result of the increased R_{pi}, which can be ascribed to the formation of a great number of grafting sites on the SA backbone through oxidation by DTA. The grafting sites, that is, SA macroradicals, induced grafting in the presence of vinyl monomers. However, an abundance of primary radicals may have accelerated the rate of termination by coupling. At the same time, an excess of DTA may have also increased the chance of an encounter between DTA and the propagating chain radicals, which would have also terminated the grafting, whereas GE remained at a high level and almost unchanged (ca. 98%), which signified the potential of this redox system.

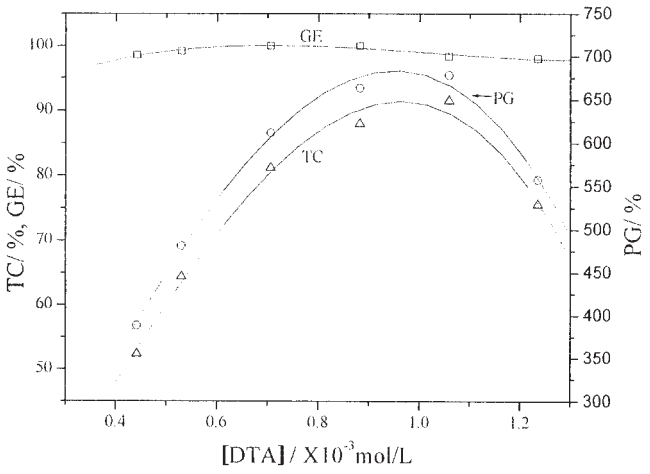

Figure 4 Effect of DTA concentrations on the grafting parameters: volume (MMA) = 1.6 mL, [SA] = 10 g/L, temperature = 25°C, and reaction time = 30 min.

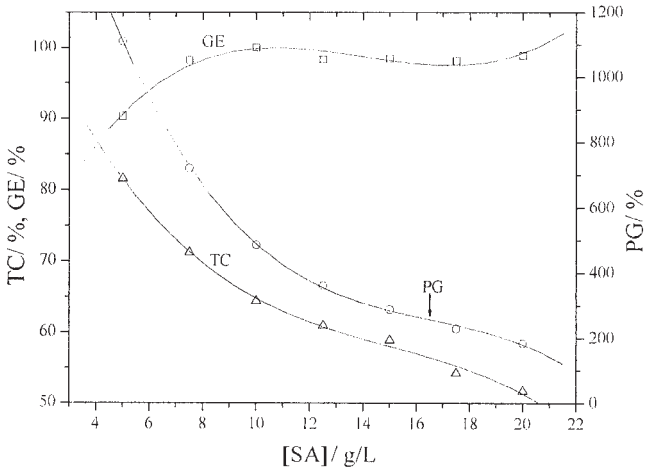

Figure 5 Effect of backbone concentration on the grafting parameters: volume (MMA) = 1.6 mL, [DTA] = 0.529 $\times$ 10^{-3} mol/L, temperature = 25°C, and reaction time = 30 min.

Effect of backbone concentration

As shown in Figure 5, with increasing SA concentration, TC and PG decreased steadily. However, GE increased first and decreased thereafter. The descending trend of TC and PG may have been due to the high viscosity of the SA solution. When the SA concentration increased, the viscous medium made the diffusion of both monomer and DTA to SA difficult; thus, the R_{gi} was greatly hindered. In addition, the difficult diffusion of DTA led to a higher local DTA concentration, which made the rate of termination accelerate due to the reaction between the propagating chain radicals and primary radicals and the oxidation of the radicals by DTA. Consequently, TC and PG decreased. In addition, the decrease in the monomer-to-backbone ratio also accounted for the decrease of PG. Similar observations[3,4] have also been reported in the ceric-induced grafting of both MMA and ethyl acrylate (EA) onto SA.

Proof of grafting

The graft copolymerization was followed gravimetrically. After exhaustive Soxhlet extraction with acetone and water alternately for 48 h to remove the homo-PMMA and unreacted SA, respectively, an insoluble solid still remained. Therefore, we confirmed that some chemical bonds must have existed between SA and PMMA; that is, we confirmed the occurrence of grafting.

The IR spectra of pure SA, homo-PMMA, and SA-*g*-PMMA were recorded to further confirm the incidence of grafting. As shown in Figure 6, in the spectrum of SA, characteristic peaks, namely, stretching vibration bands of carboxylate at 1612 cm^{-1} and hydroxyl groups at 3430 cm^{-1} were observed. In the spectrum of the graft copolymer, the aforementioned bands of SA were retained. At the same time, the bands of ester carbonyl groups appeared at 1750 cm^{-1}, and the characteristic —C—O—C— peaks of homo-PMMA appeared between 1154 and 1280 cm^{-1}. In addition, there were also peaks at 3000, between 1440 and 1497, and at 766 cm^{-1}, which were attributed to stretching vibrations of —CH_3, bending vibrations of —CH_2—, and deformation vibrations of —CH_3, respectively, which were all not present in the SA spectrum.

We also used the IR spectra analysis to prove the grafting sites by making use of the variation in the intensity of the —OH absorption band. The intensity of the —OH band in the spectrum of SA-*g*-PMMA was less than that in the spectrum of pure SA, which indicated that the grafted chains were linked through

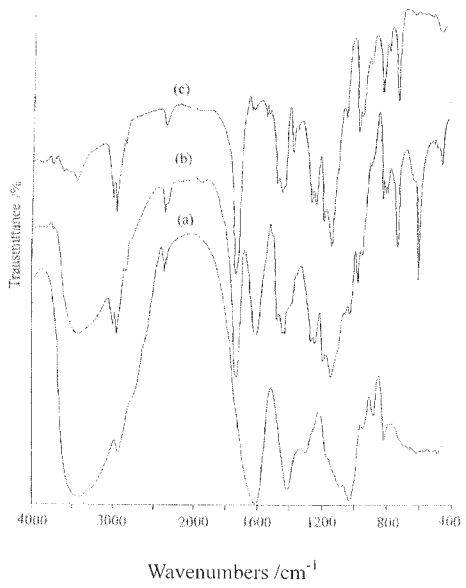

Figure 6 IR spectra of (a) SA, (b) SA-*g*-PMMA, and (c) PMMA.

the hydroxyl groups, so a tentative initiation mechanism based on a two-step, single-electron-transfer process of DTA was proposed as follows:

$$SA—OH + Ag(III) \rightarrow SA—OH^{+}\bullet + Ag(II)$$

$$SA—OH^{+}\bullet + OH^{-} \rightarrow SA—O\bullet + H_2O$$

$$Ag(II) \rightarrow Ag(III) + Ag(I)$$

$$SA—O\bullet + MMA \rightarrow \text{Initiate grafting}$$

Thermal analysis

The thermal behaviors of pure SA and the grafted copolymers were examined by a study of their TGA thermograms. The results of thermal analysis were shown in Table I. Thermal decomposition of all of the samples took place in three main steps. The first stage may have been due to the loss of adsorbed moisture and to the lactonization and/or transglucosidation of the SA part, as reported earlier.[27,28] Compared with SA, the initial weight loss of the graft copolymers was reduced, and the termination temperature of the first stage became lower. This may have been because of the incorporation of hydrophobic PMMA chains and to the decreasing amount of SA in the graft copolymers.

The second step, referred as *pyrolysis*, could be divided into two steps according to the rate of weight loss. For SA, the fast step before 276.67°C corresponded to the break of the SA backbone, and stable intermediate products were formed. The slow step thereafter was mainly attributed to the decarbonization of SA. At the same time, it is well known that a rapid decomposition of PMMA occurs between 250 and 370°C, and 100% of the product is monomer. So, the results listed in Table I were easily understandable. It is also evident from Table I that the temperature at 50% weight loss ($T_{1/2}$) of grafted SA was higher than that of ungrafted SA and increased with increasing grafting yield. So, we concluded that after it was grafted with PMMA, the thermal stability of the polymer improved.

Morphological studies (SEM)

The morphological characteristics of the grafted and ungrafted SA were studied by SEM. As shown in Figure 7, the surface of the grafted SA was more uneven than that of the pure SA. Compared with the morphology of pure SA, there was a significant increase in coagulum formation on SA-*g*-PMMA, which may have been due to the incorporation of PMMA with the SA backbone.

X-ray diffraction

To define the crystallinity of SA and SA-*g*-PMMA, X-ray diffraction patterns were analyzed, as shown in Figure 8. There was no obvious peak in the pattern of SA, and the SA was almost amorphous. However, the X-ray diffraction pattern of SA-*g*-PMMA exhibited a strengthened peak between 8.99 and 20.87° and two added small sharp peaks at about 30°. These indicated that the incorporation of PMMA improved the crystallinity of SA. The crystallinity values of ungrafted

TABLE I
Thermal Analysis Data for Ungrafted and Grafted SA

	Weight loss (%)				
		Pyrolysis			
Sample	Initial	I	II	Carbonization	$T_{1/2}$ (°C)
B	14.85 (30–185.33)	37.13 (185.33–276.67)	12.99 (276.67–568)	18.56 (568–678.33)	256.67
B_1	9.842 (30–165.33)	30.42 (165.33–291.33)	19.77 (291.33–456.67)	11.31 (518–655.33)	293.33
B_2	8.092 (30–121.33)	24.08 (200–315.33)	34.43 (315.33–423.33)	13.07 (480–580)	330

B = ungrafted SA; B_1 = 99.95% grafted SA; B_2 = 307.48% grafted SA. The temperature ranges (°C) are in parentheses.

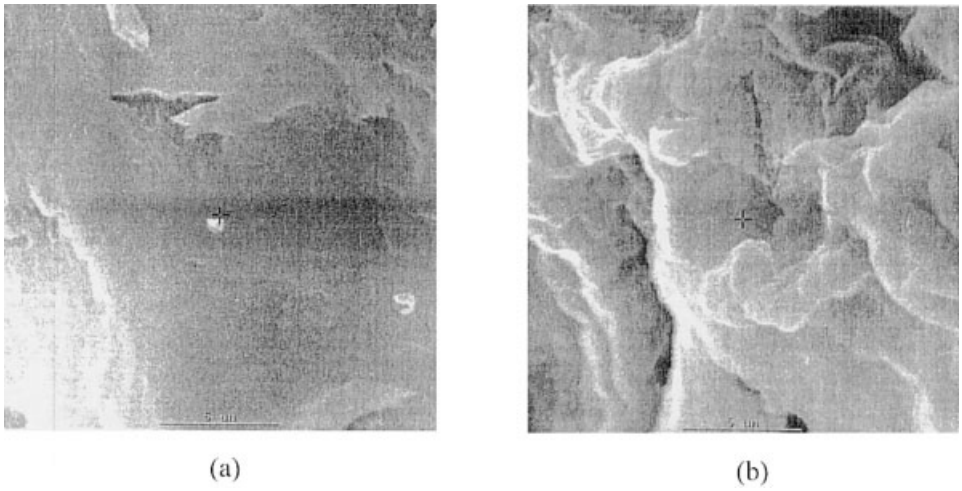

Figure 7 SEM micrographs of (a) SA and (b) SA-*g*-PMMA.

and grafted SA were calculated as 12.05 and 30.64%, respectively. The increased crystallinity of the grafted SA may provide some useful information. Further work is in progress.

CONCLUSIONS

The graft copolymerization of MMA onto SA in an aqueous alkaline medium initiated by DTA was carried out with satisfactory results. Proof of grafting was obtained from gravimetric estimation and IR analysis. On the basis of the TGA and X-ray diffraction results, we found the grafted SA to be more thermally stable and more crystallizable than the ungrafted one due to the incorporation of PMMA, which may have broadened the range of SA application. In addition, as seen from the SEM micrographs, the morphology was also changed greatly after the grafting.

In this study, graft copolymers with high GE (>90%) and PG were obtained. DTA–SA was concluded to be an efficient redox initiator for this grafting. The two-step, single-electron-transfer process mechanism of the reductive course of DTA was further confirmed. Moreover, the graft copolymerization was carried out at a mild temperature due to the lower activation energy (37.50 kJ/mol) of this grafting and in an alkali medium. This is superior to other initiators because of the solubility of SA and the insolubility of alginic acid in water. In a word, DTA as used in this initiating system is thought to be practical and has a good foreground.

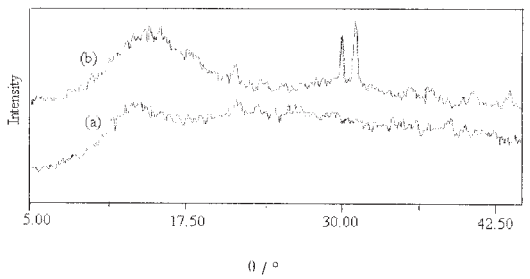

Figure 8 X-ray diffraction spectra of (a) pure SA and (b) SA-*g*-PMMA.

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