

Influence of Spacer Groups on Grafting Ability, Curing Ability, and Film Properties of Water-Based Radiation Curable Latexes

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ABSTRACT: Film-forming polystyrene/poly(*n*-butyl acrylate-*co*-glycidyl methacrylate) [PS/P(BA-*co*-GMA)] core-shell latex particles were prepared via a two-stage emulsion polymerization procedure using a PS latex seed. A delayed addition of GMA was used to locate the functional epoxy groups near the surface of the particles. The surface-bound epoxy groups were used as grafting sites for unsaturated carboxyl functional monomers having the unsaturated groups and the carboxylic group separated by 1, 5, or 10 oxyethylene units. Grafting and curing characteristics and film properties after irradiation were investigated as a function of the number of oxyethylene units. A BA-GMA [P(BA-*co*-GMA)] copolymer was used as a model system for the core-shell latex particles for quantification of the grafting reactions. The grafting was demonstrated by FTIR and ¹H-NMR spectroscopy. The effects of crosslinking was studied by thermal mechanical analysis and dynamical mechanical analysis. Differential photocalorimetry was also used for evaluation of the curing ability. It was demonstrated that the reagent having five oxyethylene units in the spacer group was grafted onto the polymer backbones to a larger extent than the other two reagents, and a more thoroughly cured film was obtained upon irradiation. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 897–906, 1998

Key words: emulsion polymerization; core-shell; water-based coatings; radiation curing; grafting reactions; spacer groups

INTRODUCTION

By using radiation technology for curing of water-borne surface coatings, the environmentally friendly nature of both technologies can be uti-

lized. The mechanical properties of the coating film will be improved by the radiation curing carried out after film formation.^{1–3}

In a previous article we presented the preparation, characterization, and curing of water-based radiation curable latexes.⁴ In that study, polystyrene/poly(*n*-butyl acrylate-*co*-glycidyl methacrylate) [PS/P(BA-*co*-GMA)] core-shell latex particles were prepared via a two-stage emulsion polymerization procedure using a PS latex seed. The morphology of PS/P(BA-*co*-GMA) core-shell

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particles was characterized by transmission electron microscopy (TEM).

The study showed that the epoxy groups present in the GMA comonomer could be utilized for the introduction of UV-reactive unsaturated groups at the particle surfaces, for example, by reaction with allyl amine and sodium acrylate, respectively. The core-shell particles carrying unsaturated groups were film forming at room temperature, and the films could be crosslinked by UV radiation as shown by an increase in stiffness and gel content and a decrease in swelling in 1-butanol.

The reactivity of a functional group may be low when it is directly attached to the main chain, which may be a result of steric hindrance by the polymer backbone and neighboring side groups. Vogl and others described the effects of spacer groups in different applications⁵⁻¹² (i.e., inert groups separating the functional groups from the backbone chain of the high polymer). Spacer groups may be either flexible or stiff. In general, spacer groups provide flexibility and allow the reactive group to react independently of the main chain.

As stated in our previous work, the use of low molecular multifunctional acrylates as crosslinkers in coatings can be avoided by incorporating the functionality needed for the crosslinking reactions into film-forming latex particles. However, the reactivity may be low due to low accessibility of the functional groups. Thus, by using spacer groups the mobility, and consequently the reactivity of the unsaturated groups needed for the radiation curing process, should increase.

The objectives of the present work were to introduce UV-reactive groups connected to flexible spacers into the shell surfaces of reactive film-forming core-shell latex particles and to study the effects of the spacers on the functionalization and curing reactions. The latex system used in the investigation was similar to that reported previously, PS/(BA-co-GMA) core-shell particles.

EXPERIMENTAL

Reagents

Styrene (S, Merck) and BA (Merck) were purified from inhibitors by passing the monomers through a column filled with active basic aluminum oxide (Merck). Hydroquinone monomethyl ether inhibitor was removed from GMA (Lancaster, U.K.) in a sim-

ilar way using neutral active aluminum oxide (Merck). The purified monomers were kept at 8°C before use. Sodium hydroxide (NaOH, Merck), sodium dodecyl sulfate (SDS, BDH), potassium persulfate (KPS, Merck), *tert*-butyl hydroperoxide (*t*-BHP, Janssen Chimica), 2,2'-azo-bis-isobutyronitrile (AIBN, Janssen Chimica), tetrabutylammonium hydroxide (Aldrich), toluene (Merck), methanol (Merck), anhydrous sodium carbonate (Merck), vanadium(IV)-oxide sulfate (Merck), hydroquinone monomethyl ether (Aldrich), triethylamine (BDH), anhydrous sodium sulfate (Acros), chloroform (Merck), and ascorbic acid (Merck) were of analytical grade and used as supplied. 2-Hydroxyethyl methacrylate (HEMA, Aldrich), polyoxyethylene-5-monomethacrylate (HEMA-5, Bimax Chemicals), polyoxyethylene-10-monomethacrylate (HEMA-10, Bimax Chemicals), and maleic anhydride (MB-Sveda) were used without further purification. The water used was deionized and distilled.

Instruments

A 200-mL calorimetric reactor (C151 Reaction Monitor, ChemiSens, Sweden) was used for the preparation of core-shell latexes.

Particle sizes for all latexes were measured by using a Coulter Model N4MD submicron particle analyzer at 20°C and at a scattering angle of 90°; the latexes were diluted with an aqueous SDS solution (3 g/L) before analysis.

FTIR spectra were recorded by using a Bruker IFS 66 instrument. Dried polymer films were dissolved in chloroform and thin films were prepared by casting the solutions onto potassium bromide disks. All spectra were recorded in the mid-IR range (4000–500 cm⁻¹) with a resolution of 2 cm⁻¹.

¹H-NMR (CDCl₃ as a solvent and tetramethylsilane as a standard) spectra were recorded on a 500-MHz Bruker ARX spectrometer.

GPC analyses were run in THF (concentration 0.1 wt %) on Waters ultra-Styragel columns (10⁵, 10⁴, and 10³ Å) using a refractive index (RI) detector. PS standards (Polysciences) were used for molecular weight calibration.

Differential photocalorimetry (DPC) analyses were run using the DPC accessory of a TA Instruments DSC 2920. A flowing helium purge at 25 mL/min was used in all analyses. Samples (0.6–1.0 mg) were analyzed isothermally at 30 and 75°C. Film samples were first kept isothermal for 10 min. The samples were then irradiated for 30 min. Before another 5-min irradiation, the sam-

ples were held isothermal for 5 min. Finally, the samples were held isothermal for 2 min.

Latex films were examined by thermal mechanical analysis (TMA) using a Mettler TMA 40 measuring cell with a Mettler TA 4000 processor. Cured and uncured film samples (7×7 mm, thickness 110–150 μm) were analyzed between -40 and $+70^\circ\text{C}$ at a constant temperature increase rate of $5^\circ\text{C}/\text{min}$, using a load of 0.05 N and a dynamic load of ± 0.025 N. The frequency used was 1/12 Hz.

Dynamical mechanical properties of the latex films were measured using a Perkin–Elmer DMA-7 with a stainless steel measuring system. Helium was used as a purge gas at 40 cm^3/min , and liquid nitrogen was used as the furnace coolant. Cured and uncured film samples (10×2 mm, thickness approximately 0.2 mm) were analyzed in tension between -70 and $+70^\circ\text{C}$ at a constant temperature rate of $4^\circ\text{C}/\text{min}$, using a frequency of 1 Hz.

Preparation of BA-GMA Copolymers

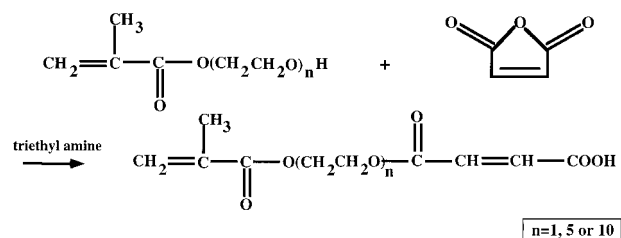
Preparation of BA-GMA copolymers was performed according to Wesslén and Wesslén.¹³ The purified monomers (60/40 BA/GMA mol ratio in feed) were dissolved in toluene (28% by weight) and AIBN (8 g/L) was added. The solution was repeatedly degassed and purged with N_2 , stirred, and kept at 67°C for 7 h. The polymer was precipitated in methanol, reprecipitated twice from toluene/methanol, and dried *in vacuo*. The product was characterized by $^1\text{H-NMR}$, FTIR, and GPC. The mole ratio of BA/GMA in the polymer was 65/35. The number average molecular weight (M_n) was evaluated from GPC chromatogram as 88,300 g/mol.

Preparation of Core–Shell Latex Particles

The details on the preparation and characterization of the core–shell particles,¹ as well as the reactor system used,¹⁴ have been described elsewhere.

PS/P(BA-co-GMA) core–shell latex particles were prepared via a two-stage emulsion polymerization procedure using a PS latex seed. A delayed addition of GMA was used in order to locate the functional epoxy groups near the surface of the particles.¹⁵

The PS seed latex was prepared batchwise in a 2-L glass reactor by emulsion polymerization at 70°C using KPS as the initiator and SDS as the



Scheme 1 Synthesis route for the preparation of MAHEMA, MAHEMA-5, and MAHEMA-10.

surfactant. The polymerization was allowed to proceed until completion. To produce core–shell particles, a second-stage polymerization at 25°C was carried out in a calorimetric reactor, which allowed close monitoring of the polymerization. PS seed latex, ascorbic acid, and vanadium(IV)-oxide sulfate were charged into the reactor. Ascorbic acid and vanadium(IV)-oxide sulfate were the components of a redox initiator system. BA, GMA, and *t*-BHP (initiator) were continuously fed to the reactor under starvation conditions. The polymerization was allowed to proceed until completion.

Preparation of Grafting Reagents

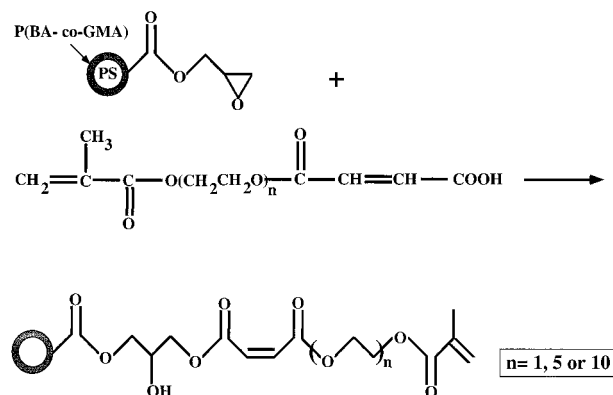
Carboxyl functional, unsaturated compounds with 1, 5, or 10 oxyethylene units in the spacer group were prepared through an addition reaction of HEMA, HEMA-5, or HEMA-10, respectively, with maleic anhydride.^{16–18}

HEMA, HEMA-5, or HEMA-10 (485, 245, or 171 mmol, respectively), maleic anhydride (968, 490, or 343 mmol, respectively), hydroquinone monomethyl ether (300 ppm), and triethylamine (600 ppm) were mixed in a 200-mL reactor.

The solution was stirred continuously under an N_2 atmosphere, and the temperature was slowly raised to 67°C and left for 7 h. The mixture was dissolved in chloroform and washed with distilled water to remove excess maleic anhydride and then dried with anhydrous sodium sulfate. The solution was then filtered and chloroform was evaporated. The procedure was repeated 5 times. The purified compounds were kept in amber glass bottles at 8°C before use. The addition reaction products of HEMA, HEMA-5, or HEMA-10 with maleic anhydride are here referred to as MAHEMA, MAHEMA-5, or MAHEMA-10, respectively. Scheme 1 presents the synthesis route for all monomers and their structures.

Modification of BA-GMA Copolymers

The BA-GMA copolymer (1 g) was dissolved in toluene (10% by weight) and heated to 75°C under



Scheme 2 Surface modification of core-shell particles using MAHEMA, MAHEMA-5, and MAHEMA-10.

stirring. Tetrabutylammonium hydroxide was added to MAHEMA, MAHEMA-5, and MAHEMA-10 in amounts equivalent to 90% of the carboxyl content. The reagents were added to the polymer solution and the reaction was allowed to proceed for 8 h (MAHEMA-5) and 12 h (MAHEMA and MAHEMA-10) at 75°C under stirring. A 10% stoichiometric excess of the reagents was used relative to the epoxy groups.

To eliminate grafting chemicals and other impurities, the grafted polymer solution was dialyzed against acetone using dialysis tubing (Spectrum®, molecular cut 12,000–14,000). The acetone was changed daily for 5 days.

Surface Modification of Core-Shell Particles

The surface-bound epoxy groups were used as grafting sites for sodium salt of MAHEMA, MAHEMA-5, or MAHEMA-10. Core-shell latex (25 mL) was charged together with SDS (final concentration 3 g/L) into a 100-mL vessel and heated to 75°C. An aqueous solution of the reagent neutralized to 90% with sodium hydroxide [5% (w/w)] and an aqueous solution of tetrabutylammonium hydroxide (10 mol % on GMA) was added dropwise to the reactor for 30 min, and the reaction was then allowed to proceed for 8 h for MAHEMA-5 and 12 h for MAHEMA and MAHEMA-10 at 75°C under stirring. A 10% stoichiometric excess of the reagents was used relative to the epoxy groups. The reaction scheme is shown in Scheme 2.

To eliminate grafting chemicals and other impurities, the reactive core-shell particles were dialyzed against an aqueous solution of SDS (2 g/L) using dialysis tubing (Spectrum®, molecular cut 12,000–14,000). The aqueous solution of SDS was changed daily for 14 days.

UV Curing

To the surface reactive core-shell latexes was added 3% (w/w on solids) of Darocur 1173 (Ciba) as a photoinitiator. The mixture was allowed to stand overnight. Films were prepared from the latexes by casting onto clean glass plates, air drying at room temperature for 3 days, and then drying at room temperature under a vacuum in a desiccator for 2 days. The films were cured by exposure to UV light from an I.S.T. Giardina cure unit. The unit contained two medium pressure mercury lamps operating at 80 W/cm. UV exposure time was 20 s for all samples. The curing of the surface reactive BA-GMA copolymers was conducted in the same way, but they were only dried in air at room temperature for 1 day.

RESULTS AND DISCUSSION

As stated in the Introduction, the main objective of the present investigation was to introduce UV reactivity into a film-forming latex system. A high glass transition temperature (T_g) core/low T_g shell latex was prepared as described previously⁴ by copolymerizing BA and GMA onto a PS seed latex using redox initiation at 25°C. By introducing the GMA monomer late in the copolymerization, the epoxy groups were primarily located in the surface regions of the particles and were available for the subsequent grafting reaction with the UV-reactive reagents.

The UV-reactive grafting reagents should have a double bond located at the end of a spacer arm and at the other end a functional group capable of reacting with epoxy groups. Derivatives of methacrylic acid fulfilling these criteria were selected. Monomethacrylates of ethylene glycol (HEMA), penta(ethylene glycol) (HEMA-5), and deca(ethylene glycol) (HEMA-10) were allowed to react with maleic anhydride to produce maleic half-esters as shown in Scheme 1. By using maleic anhydride, an additional double bond was introduced into the reagent, together with the carboxylic acid function necessary for reaction with the epoxy groups. The derivatives are referred to as MAHEMA, MAHEMA-5, and MAHEMA-10, respectively. The preparation of MAHEMA was described previously.^{16–18} In the synthesis of the oligomeric compounds, a 100% excess of maleic anhydride had to be used to achieve high yields. The conversion varied between 98% (MAHEMA) and 70% (MAHEMA-10) and the rest were unre-

acted HEMA, HEMA-5, or HEMA-10 as determined by $^1\text{H-NMR}$ spectroscopy.

The reaction of epoxy groups with carboxylic acids may take place with basic or acidic catalysts. In the present case, the grafting reaction takes place in a two-phase system (latex particles/aqueous phase) where the relatively hydrophilic reagents present in the aqueous phase should react with epoxy groups present in the latex particles. To facilitate this reaction, a phase transfer reagent, tetrabutylammonium (TBA) hydroxide, was used as a basic catalyst.

The latex particles generally become slightly crosslinked because of transfer reactions occurring during polymerization and are consequently difficult to study by NMR spectroscopy because of poor solubility. In order to more closely evaluate the grafting reactions, a model polymer similar to that in the shell [i.e., P(BA-co-GMA)] was prepared and allowed to react with the MAHEMA reagents in toluene solution with TBA hydroxide as a catalyst as discussed below.

Preparation and Modification of P(BA-co-GMA)

In order to evaluate any spacer effects on the curing ability and the film properties for the modified core-shell latexes, it is essential to know the grafting yields. A quantitative determination by NMR of the grafting yield was not possible as discussed above. A model polymer containing 35 mol % GMA was therefore prepared by copolymerizing BA and GMA in toluene solution. This copolymer was grafted in toluene solution with MAHEMA, MAHEMA-5, and MAHEMA-10 using aqueous TBA hydroxide as a catalyst. The grafting products, which have the structure of comb polymers with hydrophilic side chains, were purified by dialysis against acetone. It can be noted that washing of the toluene solutions with water resulted in toluene/water emulsions of very high stability. The polymer grafted with MAHEMA-5 was exceptionally effective, and the emulsion did not show any sedimentation for months.

The grafting of P(BA-co-GMA) with MAHEMA, MAHEMA-5, and MAHEMA-10 was demonstrated by FTIR and $^1\text{H-NMR}$. An example of a spectrum is given in Figure 1 together with a spectrum of the unmodified polymer. The spectra are normalized against the carbonyl peak. The spectrum of the grafting product shows characteristic changes attributable to the reaction of the epoxy groups with MAHEMA-5. As compared to the spectrum of the unmodified copolymers (lower curve), the modified

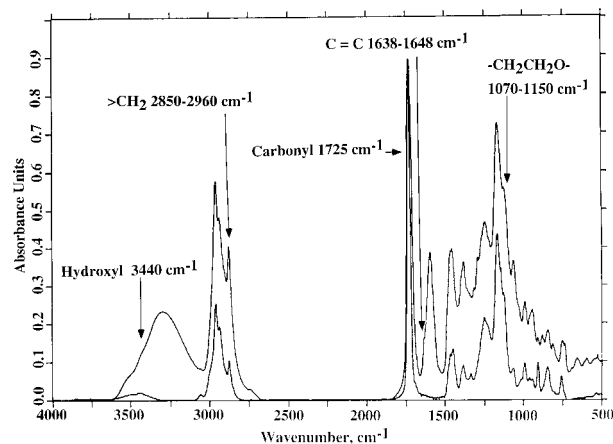


Figure 1 FTIR spectra showing unmodified P(BA-co-GMA) (lower curve) and MAHEMA-5 modified P(BA-co-GMA) (upper curve).

one (upper curve) shows an increase in the hydroxyl content and in the absorbance of carbon-hydrogen stretching. New absorbance bands that may be assigned to $-\text{CH}_2\text{CH}_2\text{O}-$ ether bonds and $\text{C}=\text{C}$ double bonds also appear in the modified spectrum.^{19,20} Because of the lack of internal reference peaks, only qualitative conclusions may be drawn from the spectra.

Because dried films of grafted P(BA-co-GMA) were insoluble, $^1\text{H-NMR}$ analyses were run on acetone solutions of the polymers diluted with CDCl_3 . The NMR spectra given in Figure 2 shows the unmodified copolymer and the copolymer modified with MAHEMA, MAHEMA-5, and MAHEMA-10. The occurrence of signals derived from $\text{CH}_2\text{CH}_2\text{O}$ groups (≈ 3.7 ppm) and the protons from $=\text{CH}_2$ ($\approx 5.6\text{--}6.3$ ppm), as well as the decrease of the signals of the epoxy groups ($\approx 2.7\text{--}3.3$ ppm), are indicative of grafting.²¹

A quantitative determination of the grafting yield was done from the NMR spectra using the integrated signals of the protons of carbon-carbon double bonds and the integrated signals of residual epoxy groups. It was shown that MAHEMA-5 needed a shorter reaction time (8 h) than MAHEMA and MAHEMA-10 (12 h) to achieve a reasonable yield (Table I).

Both FTIR and $^1\text{H-NMR}$ analyses confirm that MAHEMA, MAHEMA-5, and MAHEMA-10 reacted with the epoxy groups of the BA-GMA copolymer.

Modification and Characterization of Core-Shell Particles

In the preparation of core-shell latexes, low concentrations of surfactants have to be used. The

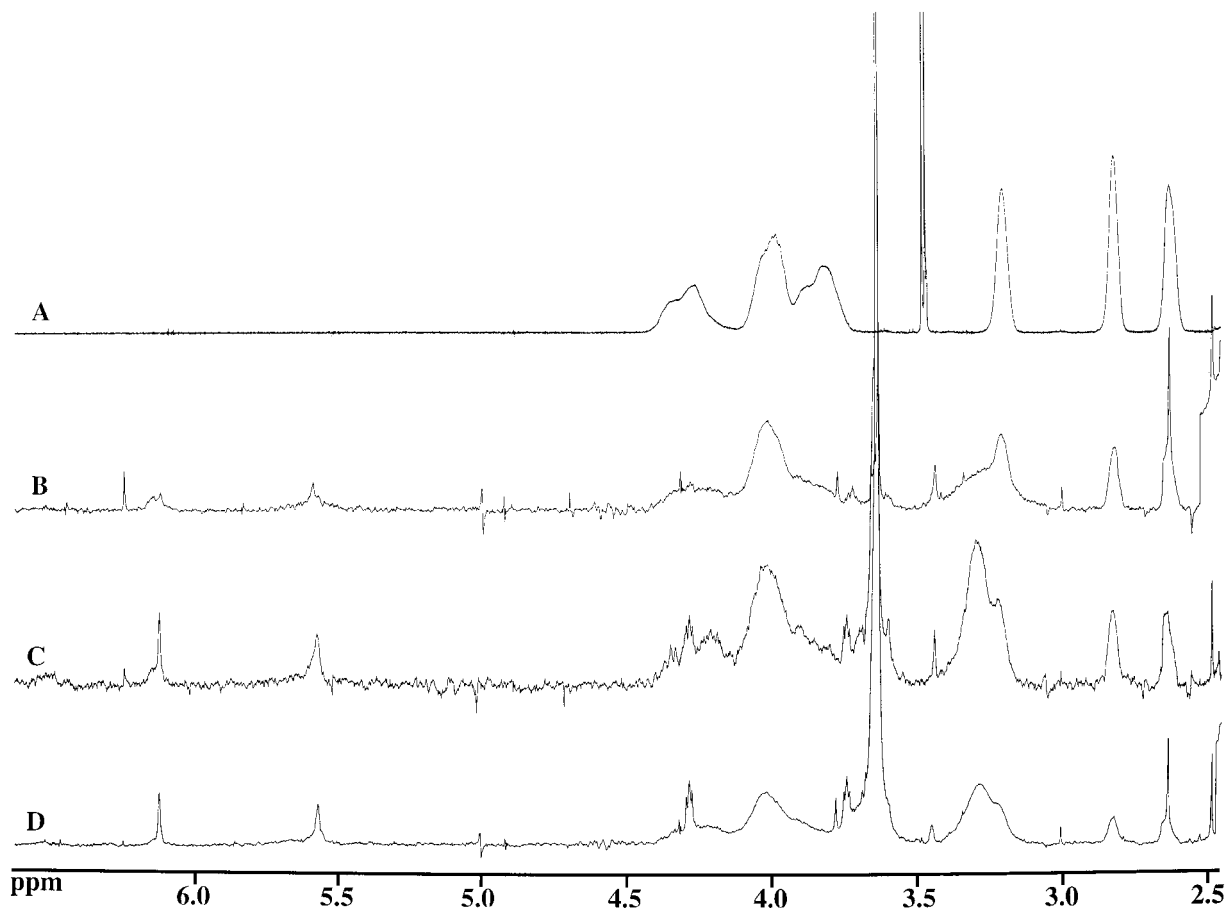


Figure 2 $^1\text{H-NMR}$ spectra showing unmodified P(BA-co-GMA) (curve A) and P(BA-co-GMA) modified with MAHEMA (curve B), MAHEMA-5 (curve C), and MAHEMA-10 (curve D).

stability of the latexes may thus be a problem in subsequent operations. In the present case extra surfactant was added to the core-shell latex to avoid agglomeration during the grafting operations. The particle diameters were checked with quasi-elastic light scattering (QELS) before and after the grafting, and only minor increases of the particle sizes were noted at the surfactant concentration used (Table II).

Table I Quantitative Determination Using $^1\text{H-NMR}$ of Grafting Yields on Grafting of P(BA-co-GMA)

P(BA-co-GMA) Modified with	Residual Epoxy/Carbon Double Bonds
MAHEMA	70/30
MAHEMA-5	60/40
MAHEMA-10	50/50

The model experiments described above showed that MAHEMA-5 was more reactive than MAHEMA and MAHEMA-10 with respect to grafting of P(BA-co-GMA). A similar difference in reactivity was also anticipated for grafting of the core-shell particles, and longer reaction times were consequently used for MAHEMA and MAHEMA-10. It can be noted

Table II QELS Measurements of Seed Latex and Unmodified and Modified Core-Shell Latex Particles

Latex Particles	Diameter (nm)
PS seed	111 \pm 29
PS/P(BA-co-GMA) unmodified	126 \pm 30
PS/P(BA-co-GMA) modified with	
MAHEMA	133 \pm 28
MAHEMA-5	128 \pm 30
MAHEMA-10	129 \pm 29

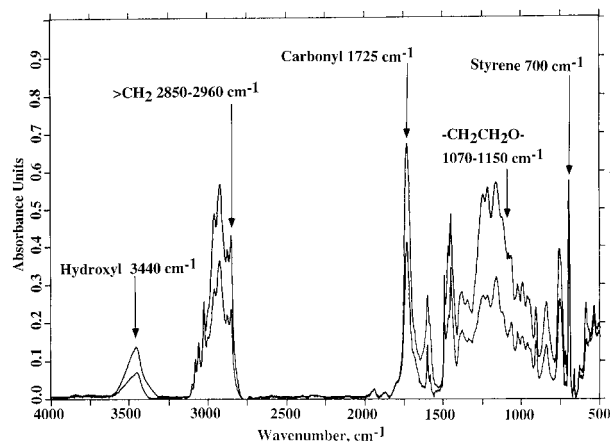


Figure 3 FTIR spectra showing unmodified PS/P(BA-co-GMA) core-shell latex (lower curve) and MAHEMA-5 modified latex (upper curve).

that TBA hydroxide was used in all grafting reactions, although MAHEMA-5 was shown to react smoothly without any phase transfer catalyst, which is a further indication of the high reactivity of this reagent. The high reactivity may be a consequence of a favorable conformation for this reagent. All grafting reactions were run at 75°C. After reaction the latexes were purified from grafting chemicals through dialysis.

The incorporation of the MAHEMA reagents into the particles was demonstrated by FTIR analysis of films prepared from the modified and unmodified latexes. The absorbance band connected to the out of plane phenyl ring vibration of PS at 700 cm^{-1} was used as an internal reference to account for variations in sample thickness and instrument recording.^{19,20}

The FTIR spectra given in Figure 3 shows characteristic changes attributable to the reaction of epoxy groups with MAHEMA-5 (see Scheme 2). As compared to the spectra of the unmodified latex (lower curve), the modified one (upper curve) indicates an increase in the content of hydroxyl groups and carbonyl groups. New absorbance bands assigned to $-\text{CH}_2\text{CH}_2\text{O}-$ ether bonds appeared. Similar differences could be seen for the reaction of epoxy groups with MAHEMA and MAHEMA-10. The FTIR analysis thus clearly shows that MAHEMA, MAHEMA-5, and MAHEMA-10, reacted with epoxy groups of the GMA residues in the shell polymer.

UV Curing of Modified Polymers

Film formation of the unmodified core-shell latexes produces a heterogeneous film consisting of

a P(BA-co-GMA) matrix and a dispersed PS phase formed by the cores. The mechanical properties of the film will be dependant on the matrix properties and, after modification, UV curing of the film should increase the stiffness of the matrix and improve the mechanical properties of the film. The curing characteristics of the modified polymers and the model system, as well as the latex, were studied by DPC, TMA, and dynamical mechanical analysis (DMA).

The heat absorbed (endotherm) or released (exotherm) by a sample during UV radiation in a temperature controlled environment, relative to an inert reference material, was registered by DPC. By this method, the energy flow and the extent of curing during radiation may be calculated, provided the number of reactive bonds is known.²²

Samples of the modified and unmodified model polymers were exposed to UV radiation in the DPC device at 30 and 75°C. A UV initiator was added to all samples. The results from the experiments are summarized in Table III. The peak maxima noted in Table III correspond to the time at which the heat flow (i.e., the curing rate) is at maximum. The model system and the latex films both behaved similarly on exposure to UV radiation. The unmodified samples did not show any reaction at all, while the modified ones cured at relatively low rates. Because of the low curing rates, neither determination of the total heat evolved during curing nor the conversion of the double bonds was possible. However, it is obvious from the peak maximum values that the curing reaction proceeded at a higher rate at 75°C as compared to 30°C, presumably due to a higher mobility of the reactive sites. Some of the samples showed two maxima, which indicates that the reaction took place in two stages. The reason for this is unclear. It was also observed that the MAHEMA-modified samples showed the highest reactivity, which may have been a result of a higher density of reactive sites in these polymers.

It may be noted that the Giardina cure unit used for curing of the samples for TMA and DMA measurements provides UV radiation of much higher intensity than the DPC instrument does, which should compensate for the low reactivity of the resins.

The mechanical properties of the unmodified and modified polymers were studied. Films prepared from the model polymer, P(BA-co-GMA) were too soft to be analyzed before irradiation. However, after irradiation, the modified samples

Table III DPC Measurements on Films Prepared from Unmodified and Modified P(BA-co-GMA) and PS/P(BA-co-GMA)

Sample	Peak Max (min)	
	30°C	75°C
P(BA-co-GMA) unmodified	No reaction	No reaction
P(BA-co-GMA) modified with MAHEMA	16	5
MAHEMA-5	>30	19
MAHEMA-10	0.13, ^a 25 ^b	0.08, ^a >30 ^b
PS/P(BA-co-GMA) unmodified	No reaction	No reaction
PS/P(BA-co-GMA) modified with MAHEMA	7	3.3
MAHEMA-5	6	0.92, ^a >30 ^b
MAHEMA-10	7	1, ^a >30 ^b

^a First peak maximum.^b Second peak maximum.

showed an increased hardness and stiffness, which clearly indicated that crosslinking had occurred.

Latex films were analyzed by TMA and DMA before and after exposure to UV radiation. The films obtained from MAHEMA-5 grafted latex particles showed the largest changes on irradiation. A large increase in the softening temperature could be noted as shown in Figure 4, as well as a decrease in the flexibility. These effects can be explained by a UV-initiated crosslinking reaction of the pendant unsaturated groups. The unmodified samples showed only minor changes on irradiation. It can also be observed that the films prepared from MAHEMA and MAHEMA-10 grafted particles behaved similarly to MAHEMA-5 on irradiation but showed a lower decrease in flexibility.

The viscoelastic behavior of polymer films are strongly influenced by the degree of crosslinking,^{23,24} and measurement of the dynamic mechanical properties for uncured and cured samples should give an insight into the crosslinking reactions. The temperature dependence of the storage modulus E' , the loss modulus E'' , and the loss tangent $\tan \delta$ were evaluated from DMA measurements. The results for the MAHEMA-5 grafted latex particles, as well as ungrafted ones, are given in Figure 5(A–D). No significant changes on UV irradiation were observed for the unmodified film [Fig. 5(A,B)]. Two distinct transitions can be observed; the first one at approximately -50°C was associated with the T_g of the PBA-rich shell polymer. The second transition at 7°C may be associated with domains in the shell

being rich in GMA. As pointed out previously, delayed addition of GMA was used in the second-stage polymerization. As is evident from the figures [5(A,B)], the mechanical characteristics of the films did not allow measurements above 50°C , and consequently no transitions associated with the T_g of the PS seed phase could be observed.

The DMA curves of the MAHEMA-5 modified samples [Fig. 5(C,D)] showed large changes on irradiation, clearly indicating that a crosslinking reaction had occurred. A significant increase in E' and a decrease in E'' over the whole temperature range was observed, and the second transition

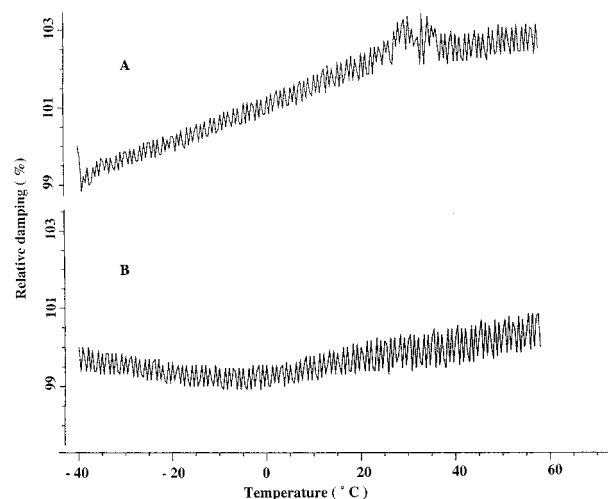


Figure 4 TMA diagram of MAHEMA-5 modified PS/P(BA-co-GMA) core-shell particles (a) before UV irradiation and (b) after UV irradiation.

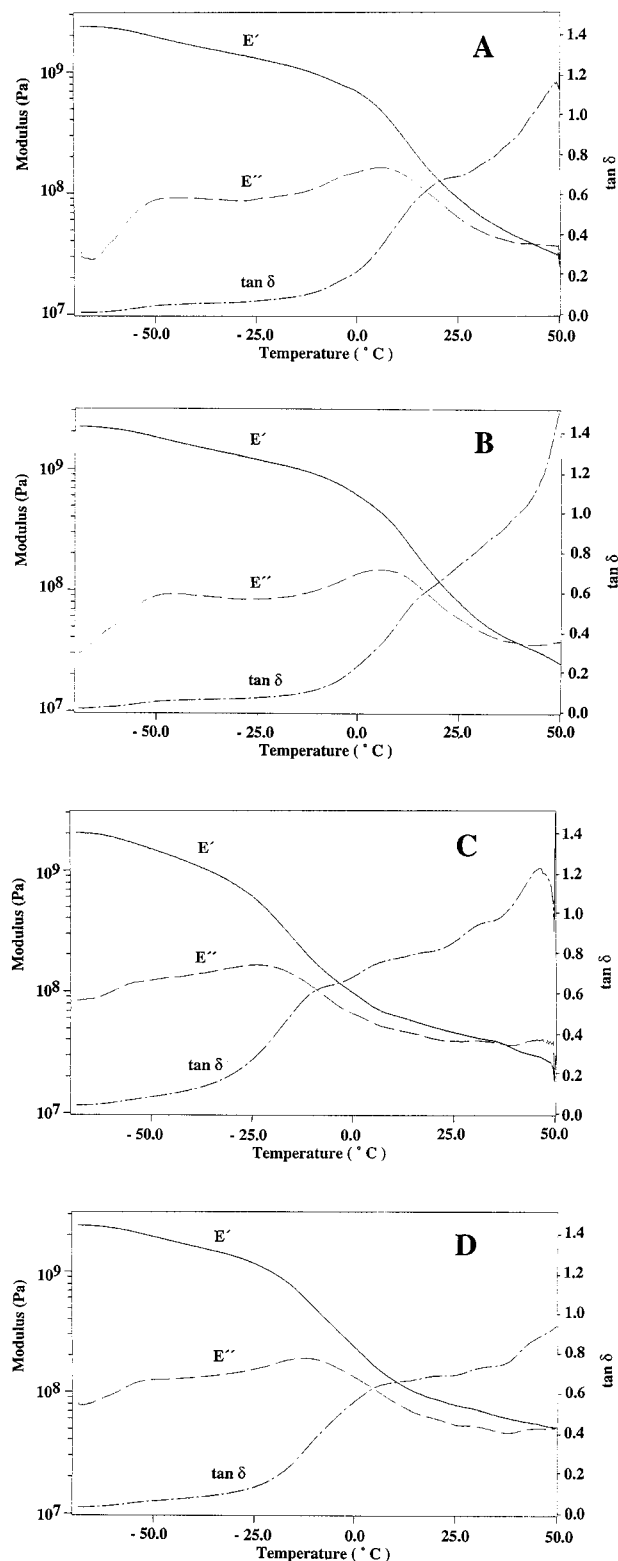


Figure 5 DMA diagram of unmodified PS/P(BA-co-GMA) core-shell particles (a) before UV irradiation and (b) after UV irradiation. DMA diagram of MAHEMA-5 modified PS/P(BA-co-GMA) core-shell particles (c) before UV irradiation and (d) after UV irradiation.

was shifted toward higher temperatures by 11°C after irradiation. Similar changes were also observed for the MAHEMA and MAHEMA-10 modified samples, but the changes were not as clear as for the MAHEMA-5 samples.

It can be noted that the second transition of the MAHEMA-5 modified latex sample occurred at a lower temperature than the corresponding transition for the unmodified sample. The reason for this shift presumably is a plasticizing effect of the oligo-oxyethylene spacer arms. A similar shift was also observed for the MAHEMA-10 grafted latex sample.

CONCLUDING REMARKS

It has been shown that the UV-reactive reagents can be prepared by reacting oligo-oxyethylene monomethacrylates with maleic acid. The reagent having a spacer arm consisting of 5 oxyethylene units, MAHEMA-5, was more easily grafted onto the BA-co-GMA backbone than those having 1 unit (MAHEMA) and 10 units (MAHEMA-10). The higher reactivity of MAHEMA-5 was also shown by the fact that no phase transfer catalyst was needed for the reaction. The high reactivity of the MAHEMA-5 reagent on grafting as compared to that of MAHEMA and MAHEMA-10 was unexpected. The reason for the high reactivity is unclear, but it may be a consequence of a favorable conformation of this reagent in the grafting reaction. Differences in solubility in the organic phase may be another reason.

Core-shell latexes containing GMA in the shells can be grafted with the reagents, and films prepared from the latexes crosslink under the influence of UV radiation as evidenced by TMA, DMA, and DPC measurements. The measurements indicated that the MAHEMA-5 grafted latex gave a more thoroughly crosslinked film than the MAHEMA and MAHEMA-10 derivatives.

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REFERENCES

1. J.-M. Loutz, W. Demarteau, and P.-Y. Herze, *Polym. Paint Colour J.*, **178**(4219), 571 (1988).
2. P. G. Garratt and K. F. Klimesch, *Polym. Paint Colour J.*, **184**(4343), 30 (1994).
3. P. H. Stenson, *Radtech Rep.*, **7**, 18 (1993).
4. J. Odeberg, J. Rassing, J.-E. Jönsson, and B. Wesslén, *J. Appl. Polym. Sci.*, **62**, 435 (1996).
5. O. Vogl, F. Xi, G. D. Jaycox, W. Simonsick, and K. Hatada, *Polymer Science, Proceedings of the 1st Pacific Polym. Conf.*, 1989 (Ed. Anderson, B. C. and Imanishi, Y.). Springer, Berlin, 1991, p. 39.
6. O. Vogl, *J. Macromol. Sci.-Chem.*, **A22**, 541 (1985).
7. O. Vogl, *J. Macromol. Sci.-Chem.*, **A21**, 1217 (1984).
8. O. Vogl, J. Muggee, and D. Bansleben, *Polym. J.*, **12**, 677 (1989).
9. F. S. Hwang and T. E. Hogen-Esch, *Macromolecules*, **28**, 3328 (1985).
10. J. Schneider, C. Erdelen, H. Ringsdorf, and J. F. Rabolt, *Macromolecules*, **22**, 3475 (1989).
11. A. Laschewsky, H. Ringsdorf, G. Schmidt, and J. Schneider, *J. Am. Chem. Soc.*, **109**, 788 (1987).
12. R. Elbert, A. Laschewsky, and H. Ringsdorf, *J. Am. Chem. Soc.*, **107**, 4134 (1985).
13. B. Wesslén and K. B. Wesslén, *J. Polym. Sci.*, **A27**, 3915 (1989).
14. H. Nilsson, C. Silvergren, and B. Törnell, *Chem. Scripta*, **19**, 164 (1982).
15. S. Magnet, J. Guillot, A. Guyot, and C. Pichot, *Prog. Org. Coatings*, **20**, 73 (1992).
16. R. E. Montgomery, Eur. Pat. 0 325 038 B1 (1989).
17. T. J. Miranda, U.S. Pat. 4,708,970 (1987).
18. I. Mani, U.S. Pat. 3,810,825 (1974).
19. S. Lee and A. Rudin, *J. Polym. Sci., Part A, Polym. Chem.*, **30**, 2211 (1992).
20. D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th ed., rev., McGraw-Hill, London, 1989, Chap. 2.
21. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th ed., Wiley, Singapore, 1986, Chap. 4.
22. I. F. Groves, T. J. Lever, and N. A. Hawkins, *Polym. Paint Colour J.*, **183**(4321), 9 (1993).
23. A. Zosel, *Polym. Adv. Technol.*, **6**, 263 (1995).
24. J. Richard, *Polymer*, **33**, 562 (1992).