

# Effect of pH on the Mechanical Properties of Functionalized Polymers Prepared by Emulsion Polymerization

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**ABSTRACT:** The influence of pH on the incorporation of a functional monomer (itaconic acid or methacrylic acid) on core-shell polymers of styrene-butyl acrylate and on their mechanical properties is investigated. The structured polymers were prepared by a two-stage emulsion polymerization process. It was found that the composition of the shell is strongly affected by the pH of the reacting medium. The amount of functional monomer that is incorporated in the shell increases as the pH decreases and becomes a maximum when the pH falls below the  $pK_a$  of the functional monomer. The mechanical properties (ultimate elongation, ultimate strength, and toughness) improve as the amount of incorporated functional monomer increases. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3299–3304, 1999

**Key words:** core-shell; functionalization; polymers; emulsion; mechanical properties

## INTRODUCTION

There is a great interest for improved emulsion-made acrylic polymers capable of forming nonporous homogeneous films. These polymers have applications in paints, adhesives, and in the manufacture of wax, paper, textile, and other materials of daily use.<sup>1–3</sup> To improve their mechanical properties and to increase their compatibility with other materials as well as their adhesion to substrates, especially those that are prone to corro-

sion, acrylic polymers are usually modified with small amounts of a functional monomer such as *N*-methylolacrylamide, acrylic acid, methacrylic acid (MA), or itaconic acid (IA).<sup>4–10</sup>

The incorporation of the functional monomer in the polymer is controlled by its distribution between the aqueous phase and the reacting particles and by the relative reactivities of the participant monomers.<sup>4,8,10</sup>

Rios et al.<sup>10</sup> synthesized core-shell polymers of styrene and butyl acrylate containing different concentrations of MA. These authors found that the amount of MA incorporated in the polymers (mostly in the shell) modified the particle morphology and the mechanical properties of the polymeric films. However, they did not investigate the role of pH on the synthesis and composition of such materials.

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**Table I Formulations Used to Prepare Functionalized Core-Shell Polymers**

Reagents	First Stage	Second Stage
Distilled water (mL)	700	50
SDS (g)	1.72	—
KPS (g)	0.3	0.45
St (mL)	30	—
ALMA (mL)	0.64	—
AB (mL)	—	45
IA or MA (g)	—	Variable

This study investigates the influence of pH of the reacting medium on the incorporation of a functional monomer (either MA or IA) on core-shell polymers of styrene and butyl acrylate, synthesized by a two-stage emulsion polymerization process, and on their mechanical properties.

## EXPERIMENTAL

Reagent grade styrene (St) from Scientific Polymer Products (Ontario, NY, USA) (SPP) was passed through a DTR-7 column (SPP) to remove the inhibitor. Reagent-grade butyl acrylate (BA) from SPP was further purified by vacuum distillation. The crosslinking agent was industrial-grade allyl methacrylate (ALMA), which was used as received. Itaconic acid (IA) and methacrylic acid (MA) were analytical grade from Aldrich (Milwaukee, WI, USA). Sodium dodecylsulfate (SDS) and potassium persulfate (KPS), from Aldrich, had purities greater than 99%. Water was deionized and doubly distilled.

Core-shell polymers were synthesized by a two-stage emulsion polymerization process. Formulations are given in Table I. In the first stage, St was polymerized at 60°C in the presence of small amounts of ALMA to produce slightly crosslinked particles that were used as seeds for the second stage. The conversion after 2.5 h of reaction was around 92%. In the second stage, BA and aqueous solutions of KPS and either IA or MA were added continuously during 15 min to the polystyrene latex. The reactions in the second stage were carried out at different pH values for 2.5 h with conversions larger than 93%. A pH of 2.0 was obtained simply by adding IA or MA without any buffer. Other pH values were obtained by the addition of a buffer of NaH<sub>2</sub>PO<sub>4</sub> and NaHPO<sub>4</sub> (pH = 5.0–6.0) or NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> (pH = 7.5–10.0). The polymer was recovered from the latex

by freezing and filtration. The product was washed to eliminate adsorbed surfactant and unreacted monomer, and dried in a vacuum oven.

Glass transition temperatures ( $T_g$ ) were determined with a Mettler TC15 differential scanning calorimeter at a scanning rate of 10°C/min and with a PL-DMTA MK II torsion rheometer using parallel plates at a frequency of 0.3 Hz.

The amount of MA or IA incorporated into the polymer was determined with a Nicolet (Madison, WI, USA) 5ZDA FTIR spectrometer, equipped with an Attenuated Transmitted Reflectance accessory; and by potentiometric titration of the latex and of the aqueous phase obtained after breaking the emulsion and removing the organic phase.

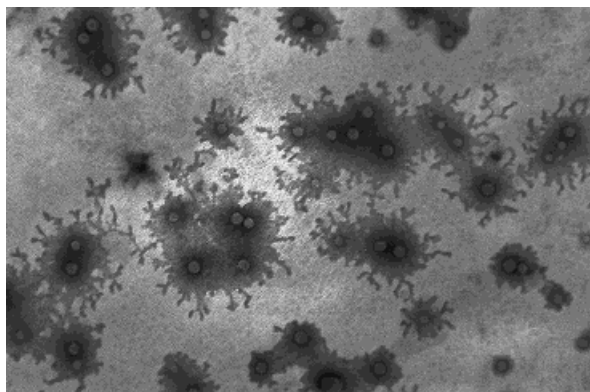
Particle size was measured at 25°C with a Malvern (Worcestershire, UK) 4700C quasi-elastic light scattering (QLS) apparatus. Examination of the samples was performed in a JEOL-100CX (Sundbyberg, Sweden) transmission electron microscope (TEM) operating at 80 keV to diminish radiation damage to the specimens.

Polymer bars (11 × 12 × 0.3 cm) for mechanical and DMTA measurements were made by heating (120°C) and pressing (125 bars) the sample in a hydraulic press. Tensile tests were performed at room temperature in a Universal Testing Machine (United) (Garden Grove, CA, USA) according to the ASTM D-638 method at an elongation speed of 3 inches/s. The impact resistance was determined by the ASTM D-1709 method. Hardness was measured with a Shore-A hardness instrument.

## RESULTS AND DISCUSSION

Formation of core-shell particles was confirmed by TEM and QLS. A representative TEM photograph of the latex prepared with IA at a pH of 2.0 is depicted in Figure 1. The polystyrene core is clearly observed, whereas the shell appears spread around the nuclei because of the melting and subsequent fusion of the shells of neighboring particles caused by exposure to radiation.

The average particle sizes (measured by QLS) at the end of the first and the second stages are reported in Tables II and III. Particles have average diameters around 75 nm at the end of the first stage, and then they grow following the addition of BA with or without the functional monomer (second stage). This suggests that a layer of poly(butyl acrylate) (PBA) or poly(butyl acrylate-



**Figure 1** TEM photograph of a St/MMA/IA core-shell latex prepared at pH = 2.0.

co-functional monomer) grows over the polystyrene particles used as seeds. A simple calculation shows that an increase of around 20 nm is expected at the end of the second stage if all the PBA is incorporated over the seeds. However, when a basic pH is used, particles grow more than expected, probably because of particle coagulation caused by the decrease of the electrical double layer by the salt of the functionalizing monomer in the aqueous phase. This effect is more important with IA because this monomer can form a divalent salt at basic pH values, which can more effectively decrease the electrical double layer of the polymeric particles.

The storage modulus of the core-shell polymers functionalized with MA as a function of temperature for different pH values is shown in Figure 2. In all samples, the storage modulus is high ( $\sim 10^9$  Pa) at the lowest temperature examined ( $-100^\circ\text{C}$ ). This value is typical of glassy polymers.<sup>11</sup> As the temperature increases, the storage modulus decreases, first slowly and then more rapidly as the glass transition temperature ( $T_g$ ) of the polymer with the lowest  $T_g$  (polymer in the

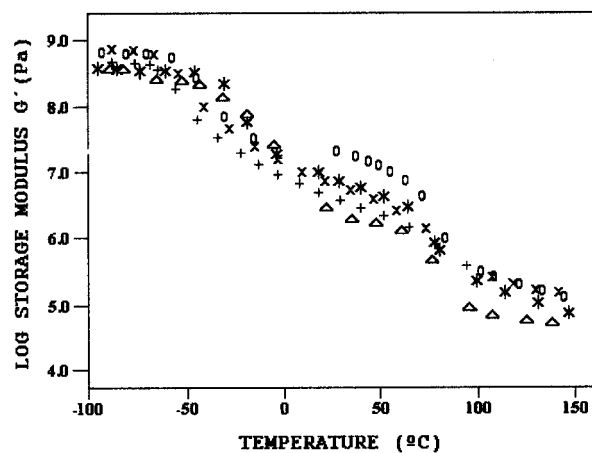
**Table III Particle Size as a Function of pH of Functionalized St(ALMA)/BA/MA Core-Shell Polymers**

pH	End of First Stage (nm)	End of Second Stage (nm)
2.0	64	83
3.0	70	88
6.0	63	81
8.5	73	99
10.0	77	108

shell) is approached. The low-temperature  $T_g$  of the structured polymer prepared at a pH of 2.0 appears at  $-29^\circ\text{C}$ . As the pH is increased, this  $T_g$  shifts to lower temperatures (Table IV). The structured polymers prepared at a pH equal to or higher than 6.0 have a  $T_g$  similar to that of PBA ( $\sim -50^\circ\text{C}$ ).<sup>12</sup> Inasmuch as the glass transition temperature of the poly(methacrylic acid) (PMA) is much higher than that of PBA,<sup>12</sup> it is clear that at low pH values, MA is incorporated in greater amounts in the shell to form poly(butyl acrylate-co-methacrylic acid). However, as the pH of the reacting medium is increased, the  $T_g$  of the shell approaches that of the PBA, suggesting that the amount of MA incorporated into the outer layer of the particle decreases significantly, that is, the shell is composed mainly of PBA. MA has a  $\text{p}K_a$  of 4.5,<sup>13</sup> which means that at a pH larger than this value, the equilibrium is displaced to the salt species. Since the salt of MA is much more soluble in the aqueous phase than in the organic phase

**Table II Particle Size as a Function of pH of Functionalized St(ALMA)/BA/IA Core-Shell Polymers**

pH	End of First Stage (nm)	End of Second Stage (nm)
Without IA	79.2	98.0
2.0	79.2	90.3
5.0	79.6	103.0
7.5	79.6	221.0
8.5	79.6	215.0



**Figure 2** Storage modulus-temperature curves for the St/MMA/MA core-shell polymers prepared at different pH values: (×) 9.5; (+) 8.5; (o) 6.0; (\*) 3.0; (Δ) 2.0.

**Table IV** Glass Transition Temperatures of Structured Polymers of St(ALMA)/BA/MA Measured by DSC

pH	$T_g$ (Core) (°C)	$T_g$ (Shell) (°C)
Without MA	-52	102
2.0	-29	109
3.0	-29	107
6.0	-42	102
8.5	-49	106
10.0	-49	107

and less reactive than MA, the salt should be incorporated in much smaller amounts in the particle than its acid counterpart.

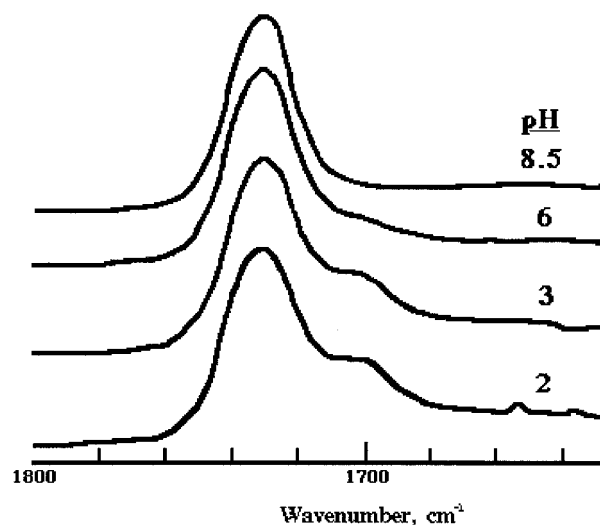
A second  $T_g$ , signaled by the second drop in the storage modulus (Fig. 2), is detected at higher temperatures (100°C), which evidently belongs to the polystyrene forming the core.<sup>12</sup> The presence of two glass transition temperatures clearly demonstrates that two distinguishable domains exist in these structured polymers: a shell composed of PBA containing a certain amount of MA, depending of the pH used, and a core made of polystyrene.

Similar conclusions can be drawn for the structured polymers prepared with IA as a function of pH (Table V). In this case, however, the glass transition temperature of the shell becomes similar to that of the PBA at lower pH values because the first  $pK_a$  of this monomer is only 3.5.<sup>13</sup> Hence, the sodium salt of IA forms at lower pH values. Only the material prepared at a pH (2.0) smaller than the  $pK_a$  of IA has a glass transition temperature (-42°C) higher than that of PBA.

Figure 3 shows partial IR spectra of core-shell polymers made with MA. At a pH of 8.5, only the band at 1730  $\text{cm}^{-1}$  of the  $\text{COO}^-$  groups of PBA is observed. However at lower pH values, the  $\text{COO}^-$  band of PMA at 1700  $\text{cm}^{-1}$  is detected as a small shoulder. Moreover, this band becomes more in-

**Table V** Glass Transition Temperatures of Structured Polymers of St(ALMA)/BA/IA Measured by DSC

pH	$T_g$ (Core) (°C)	$T_g$ (Shell) (°C)
2.0	-42	109
5.0	-52	102
7.5	-51	106
8.5	-54	107

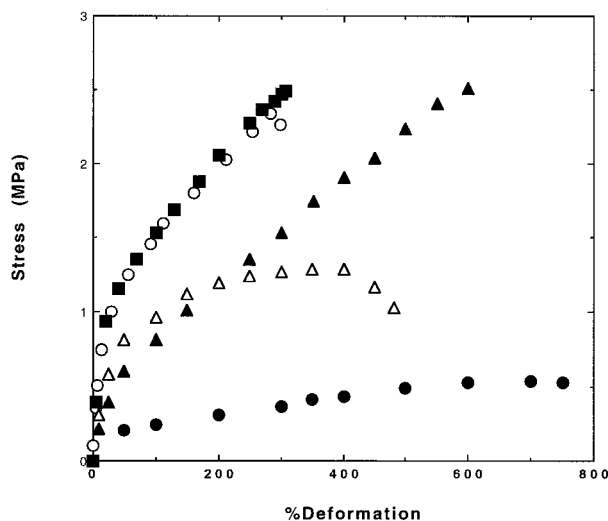
**Figure 3** Infrared spectra of St/MMA/MA core-shell polymers prepared at different pH values.

tense as the pH decreases. These results indicate PMA is incorporated into the shell as the pH decreases, particularly when the pH is lower than the  $pK_a$  in agreement with the DSC measurements.

The incorporation of the functional monomer was also confirmed by potentiometric titration. At low pH values, around 33% of the IA is incorporated in the polymer, whereas only 11% and 1% were incorporated at neutral and basic pH, respectively. For MA, around 75% of the acid is incorporated at acid pH, 35% at pH equal to 6.0, and practically none at basic conditions.

Figure 4 shows stress-strain curves for St/BA/MA structured polymers synthesized at different pH values. For comparison, tests were also performed with core-shell polymers of similar St/BA composition but without functional monomer. The presence of the functional monomer increases the mechanical properties of the core-shell polymers. When the second polymerization stage is carried out at conditions where the incorporation of PMA (pH = 2.0) is favored, a more rigid material is obtained. As the pH is increased, the material becomes less rigid and exhibits a larger deformation to rupture and lower ultimate strength because less amount of MA is incorporated in the shell. The material prepared without functionalizing agent is the less rigid and exhibits the lower ultimate strength and the higher deformation to rupture.

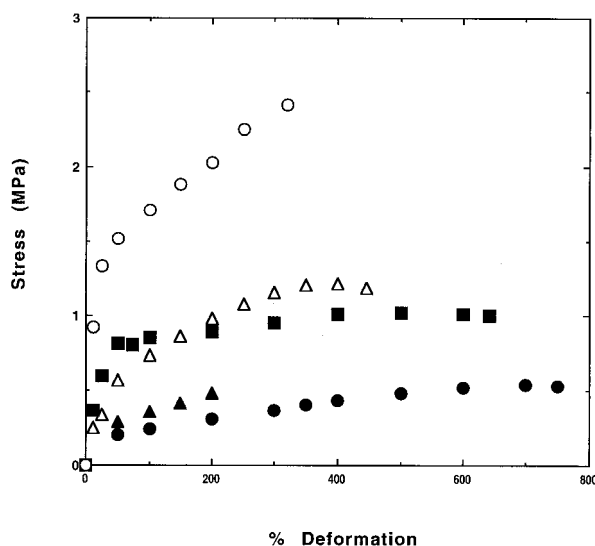
Similar behavior is observed with St/BA/IA structured polymers (Fig. 5). Here, too, the addition of IA makes the material more rigid and



**Figure 4** Stress-strain curves for St/BA/MA polymers synthesized at different pH values: (○) 2.0; (■) 3.0; (▲) 6.0; (△) 8.5; (●) without MA.

increases its ultimate strength and decreases its deformation to rupture. Just like the polymer functionalized with MA, the maximum stress decreases and deformation to rupture increases as the pH is increased.

Tables VI and VII show the results of the tests of impact resistance and Shore type "A" hardness of the core-shell polymers. Impact resistance and hardness increase with the amount of functional monomer incorporated in the shell. The material



**Figure 5** Stress-strain curves for St/BA/IA polymers synthesized at different pH values: (○) 2.0; (■) 5.0; (▲) 7.5; (△) 8.5; (●) without IA.

**Table VI** Impact Energy and Shore "A" Hardness as a Function of pH for Functionalized Core-Shell Polymers of St(ALMA)/BA/IA

pH	Impact Energy (J/cm)	Hardness Shore "A"
Without IA	22.0	72.0
2.0	36.7	83.8
5.0	33.2	66.3
7.5	21.0	71.0
8.5	26.2	55.1

prepared at the lowest pH (pH = 2.0) presents the highest impact resistance and hardness. The combination of a more rigid material with a good impact resistance makes the material prepared at pH = 2.0 potentially interesting for many applications.

## CONCLUSIONS

Our results indicate that the composition of the shell of St/BA/MA or St/BA/IA core-shell polymers is strongly affected by the pH of the reacting medium during the second stage. At pH values below the  $pK_a$  of the functional monomer, more is incorporated in the outer layer of the particle. As the pH is increased, the formation of the salt of the acid monomer is favored and since this species is more water soluble and less reactive, the incorporation of the functional monomer into the particle diminishes. Hence, in this case, the shell is composed mainly of PBA. As expected, these changes in composition in the outer layer affect the stress-strain behavior, the impact resistance, and the hardness of the materials. The material

**Table VII** Impact Energy and Shore "A" Hardness as a Function of pH for Functionalized Core-Shell Polymers of St(ALMA)/BA/MA

pH	Impact Energy (J/cm)	Hardness Shore "A"
2.0	33.0	84.0
3.0	30.1	72.6
6.0	24.2	71.1
8.5	23.6	73.4
10.0	24.8	71.5

prepared at lower pH values proves to be more rigid and tougher.

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