

Ionomer Synthesis by Emulsion Polymerization of Styrene and Sodium Acrylate

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ABSTRACT: The emulsion copolymerization of styrene and sodium acrylate is reported using either a water-soluble initiator (potassium persulfate, or KPS), or an oil-soluble one [2,2-azoisobutyronitrile (AIBN)]. Reaction rates are fast with both KPS and AIBN. With KPS, conversions >90% are achieved in 50 min, with AIBN, conversions reach 85% in 100 min. Particle size, measured by quasielastic light scattering (QLS), increases with conversion. Particle size in final latices is ~ 70–80 nm. Copolymer formation is confirmed by infrared (IR) spectroscopy, plasma emission spectroscopy (PES), and scanning electron microscopy (SEM). IR and PES indicate that mainly sodium acrylate reacts at the beginning of the reaction and then styrene is incorporated in the copolymer backbone. The copolymer produced with KPS contains more sodium acrylate than the one made with AIBN. These differences can be explained in terms of the reactivities and partitioning (local concentrations) of the monomers and of the type of initiator used. Thermomechanical analysis (TMA) of the copolymers reveals two transitions: one at ~ 100°C, which is due to the glass transition temperature (T_g) of polystyrene blocky segments in the copolymer, and another one at higher temperatures, which is associated to the T_g of segments composed of alternated sodium acrylate and styrene units. The higher-temperature transition shifts to lower values as the reaction proceeds because these segments become richer in styrene. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 879–889, 1997

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INTRODUCTION

Even though the commercial use of styrene-based ionomers has not expanded, their study has largely contributed to a better understanding of ion-containing polymers.¹ Ionomers possess unusual properties not seen in conventional polymers, which arise from the complex electrostatic interactions among charged-groups and the van der Waals interactions among the polymer back-

bones.^{2,3} As a result of such interactions, ionic polymers form a variety of microstructures in solution.^{4,5} The understanding and modeling of ionomer microstructure are, at present, areas of active research.

High levels of ionization in inorganic polymers provide a wide range of useful properties. However, the effect of the ionic forces in organic polymers containing high levels of ions and no plasticizers is too drastic to yield useful mechanical properties. In fact, they become brittle and intractable.⁶ By contrast, at low levels of ion concentration, useful modifications in the properties of organic polymers can be produced.⁷ Polymers containing low concentrations of ions can be synthesized by the copolymerization of a conventional,

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nonionic monomer with small amounts of an ionic or an ionizable monomer; in the latter case, a partial or complete neutralization is required.^{8–12} Alternatively, a chemical modification of conventional polymers, such as treatment of poly(ethylene-co-propylene-codiene) (EPDM) or polystyrene with sulfonating agents followed by partial neutralization after treatment, can yield useful partially ionic polymers.¹³ Considerable attention has been devoted to the development of polymers of this nature.

Ionomers' applications are based either on the ionic aggregation (i.e., cluster formation) or on the interaction of polar groups of other polymers with the ionic aggregates. Such applications include enhanced elastomeric green strength, enhanced melt viscosity and toughness, water-based pressure-sensitive adhesives, and improved oil-resistance in packaging materials.^{14,15}

In this article we present the direct synthesis of low-ionic-content polystyrenes by emulsion copolymerization of styrene (ST) and sodium acrylate (SAc) using a water-soluble initiator (potassium persulfate) or an oil-soluble one 2,2-azobutyronitrile (AIBN). The kinetics of polymerization, followed by a battery of techniques, which includes compositional analysis and particle size as a function of reaction time, demonstrate that the location and concentration of monomers and of the initiator have a strong influence on the composition and structure of the resulting copolymer. Copolymers were studied by thermomechanical analysis (TMA) to provide a hint on the structure of the material and to investigate the effect of the ionic monomer on the mechanical properties of the resulting materials.

EXPERIMENTAL

Reagent-grade styrene (Scientific Polymer Products, Ontario, NY) was passed through a DTR-7 column (SPP) to remove the inhibitor before use. Sodium acrylate (Polyscience, Warrington, PA) with purity > 99% was used as received. Sodium dodecylsulfate (SDS) from Tokyo Kasei had a purity > 99%. Potassium persulfate (KPS) and hydroquinone were reagent-grade from Productos Químicos, Monterrey. AIBN from Du Pont (Wilmington, DE) was recrystallized from methanol. Reagent-grade toluene (Merck, Rahway, NJ) and doubly distilled water were used.

Polymerization was carried out at 60°C in a 2-L glass reactor. The weight ratio of styrene to

sodium acrylate (ST/SAc) was variable 80 : 20, 90 : 10, and 95 : 05). The weight ratio of water to monomers was kept equal to 10 : 1. SDS concentration was 0.018M, which is twice its critical micellar concentration.¹⁶ The reaction vessel was charged with SDS aqueous solution and heated to 60°C with continuous agitation and N₂ bubbling. After 5 min, monomers were added to form the emulsion, and then a concentrated aqueous solution of KPS (or a concentrated solution of AIBN in styrene) was added. A variation of this procedure consists in adding first sodium acrylate and 15 min later styrene, to promote the formation of poly(sodium acrylate) seeds where styrene can react. Samples were taken at different stages of reaction and quenched by cooling and adding a 0.05M hydroquinone aqueous solution. Samples were then put in a vacuum oven to evaporate the volatiles. The solid residues were then washed exhaustively with hot water, methanol, and toluene to remove unreacted sodium acrylate and non-adsorbed surfactant as well as any poly(sodium acrylate) or polystyrene that may have formed during the reaction. Alternatively, polymer was isolated by precipitation. Here latex samples were treated with a 0.14M Al₂(SO₄)₃ aqueous solution to break the emulsion, filtered, washed with hot water, methanol, and toluene, and dried. The agreement between both techniques is within 96%. Samples used for compositional analysis by plasma emission spectroscopy (PES), scanning electron microscopy (SEM), and FTIR spectroscopy were further purified by dialysis for 24–48 h.

Copolymer composition was followed by PES. Here, samples of known weight (0.1–1 g) were calcinated for 4 h in a muffle at 550°C. The resulting ashes were dissolved in a 3 wt % HCl solution. The sodium content in these samples was determined with a P FMA-03 Spectraflame from Spectro Analytical Instruments (Fitchburg, MA). The sodium content in the copolymers was also measured with a JEOL JSM 5400LV scanning electron microscope equipped with a quantum super dry detector. FTIR analysis was done in pellets formed with FTIR-grade KBr (Aldrich, Milwaukee, WI) in a Nicolet 5ZDA FTIR spectrometer.

Quasielastic light scattering (QLS) measurements were made with a Malvern 4700 QLS apparatus equipped with an He–Ne ion laser ($\lambda = 644$ nm). The measured diffusion coefficients were represented in terms of apparent radii by means of Stokes law assuming that the solvent has the viscosity of water. Latices were diluted up to

100 \times and filtered through 0.2- μm Millipore filters before QLS measurements to minimize particle-particle interactions and to remove dust particles.

Average molecular weights and molecular weight distributions (MWD) were measured with a Perkin-Elmer LC 30 size exclusion chromatograph equipped with a LC30 refractive index detector and a Dawn multiangle light scattering detector from Wyatt Technology (Santa Barbara, CA). Columns with molecular weights ranging from 10^5 to 10^7 were employed.

Thermal transitions of homopolymers and copolymers were examined in the compression mode with a Perkin-Elmer TMA 7 thermomechanical analyzer with a heating rate of $5^\circ\text{C}/\text{min}$. For these tests, samples were molded in the shape of cylinders of 2 cm in diameter and 0.03 cm in height.

RESULTS

Figure 1 shows overall conversion as a function of time for the copolymerization of styrene and sodium acrylate initiated with KPS (0.0075 w/w monomers) for two different ST/SAc ratios. In both cases, fast reaction rates and high conversions are achieved ($>90\%$) in < 50 min. Notice that the initiation stage is very short and that no induction period is observed. The reaction rate is faster when the initial amount of sodium acrylate in the monomer feed is higher. Particle size as a function of time is shown in the inset of Figure 1. The evolution of particle size follows closely the conversion curve: first, particles grow rapidly up to ~ 40 min and then their size remains constant. However, particle size is not influenced by the ST/SAc ratio.

Figure 2 depicts overall conversion and particle size (inset) as a function of time for the copolymerization initiated with AIBN (0.01 w/w monomers) for two different ST/SAc ratios. The polymerization rate is slower and conversions are lower than those observed with KPS (Figs. 1 and 2). Again, reaction rate and final conversion depend on the initial monomers ratio: faster rates and higher conversions are attained when the amount of sodium acrylate in the feed is larger. Latex particles grow with conversion until most of the monomers have been consumed, then particle size remains constant afterward (inset in Fig. 2).

Table I reports copolymer composition obtained by PES as a function of time for the copolymerizations reported in Figures 1 and 2 for the ST/SAc ratio of 90 : 10. Regardless of the type of initiator

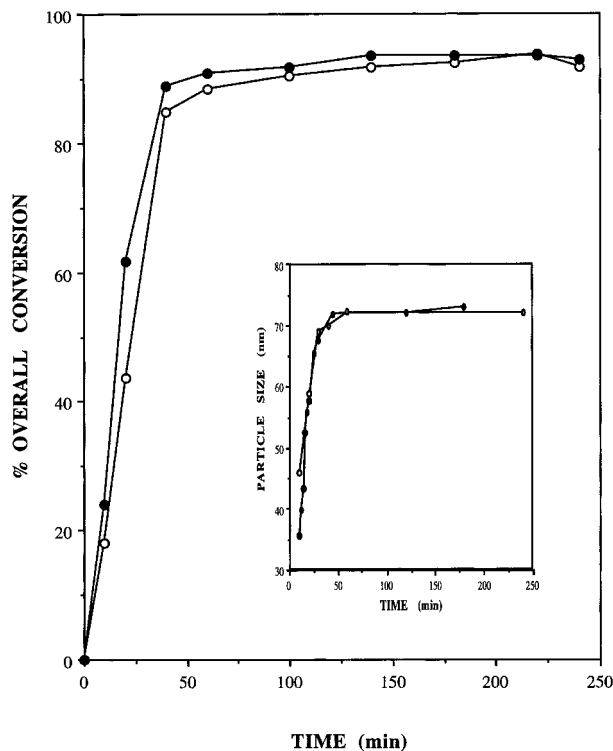


Figure 1 Overall conversion as a function of time for the emulsion polymerization of styrene (ST) and sodium acrylate (SAc) initiated with potassium persulfate at 60°C for two different ST/SAc ratios: (○) 95 : 5; (●) 90 : 10. Inset: particle size as a function of time for the reactions shown in the figure.

used, copolymer composition is richer in sodium acrylate at early stages of reaction and, as the reaction proceeds, the copolymer becomes richer in styrene. Also, copolymers synthesized with KPS contain more sodium acrylate at any stage of the reaction than those produced with the water-insoluble initiator, AIBN. Hence, the concentration and location of monomers and of the initiator (or the free radicals that are produced) appear to have a profound effect on the polymerization kinetics.

The effect of KPS concentration on the polymerization kinetics is shown in Figure 3. Here, the ratio of ST/SAc was maintained constant (90 : 10). Reaction rates and final conversions increase as the concentration of KPS is increased, as expected from the theory of emulsion polymerization,¹⁷ since the flux of free radicals and the probability of particle nucleation increase with increasing concentration of initiator. Likewise, particle size must decrease as the concentration of initiator is increased because of the larger number of particles generated. In fact, particles become

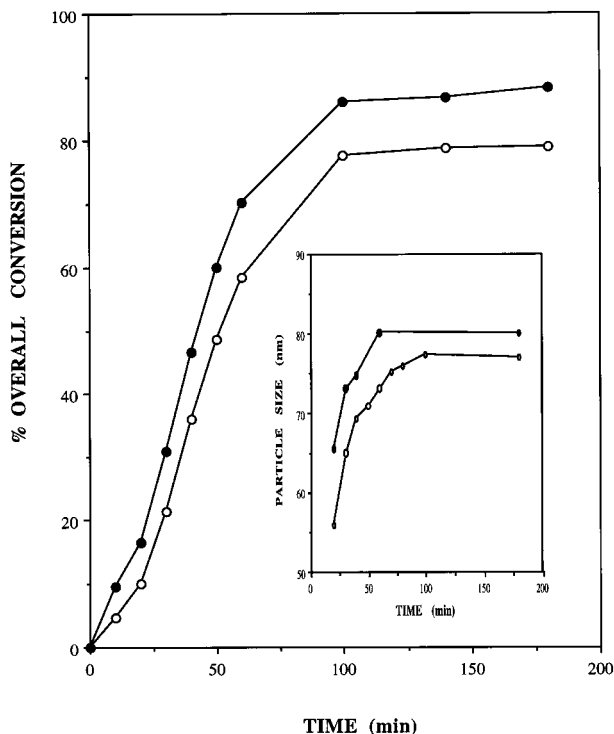


Figure 2 Overall conversion as a function of time for the emulsion polymerization of styrene (ST) and sodium acrylate (SAc) initiated with AIBN at 60°C for two different ST/SAc ratios: (○) 95 : 5; (●) 90 : 10. Inset: particle size as a function of time for the reactions shown in the figure.

smaller with increasing KPS concentration (inset in Fig. 3). Again, the evolution of particle size closely follows the conversion curve.

Similar effects on polymerization rate and conversion for the polymerization of ST/SAc (90 : 10) are observed when the concentration of AIBN is varied (Fig. 4). Reaction rates and conversions increase, whereas particle size diminishes (inset in Fig. 4) as the concentration of AIBN is increased. However, reaction rates are slower and

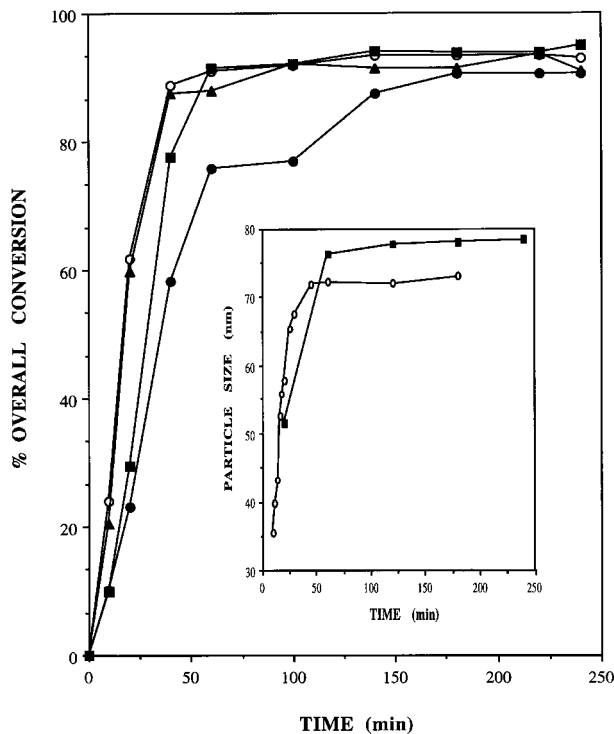


Figure 3 Overall conversion as a function of time for the emulsion polymerization of styrene and sodium acrylate (ST/SAc = 90 : 10) initiated at 60°C with different concentrations of potassium persulfate: (●) 0.0018; (■) 0.0028; (▲) 0.0065; (○) 0.0075 in w/w monomers. Inset: Particle size as a function of reaction time for the reactions indicated with the same symbol.

conversions are lower with AIBN compared to those obtained with KPS (Figs. 3 and 4). Notice that the initiation stage is fast and that polymerization rate in this stage appears to be independent of initiator concentration.

Average molecular weights of final copolymers as a function of the initial ST/SAc ratio are reported in Table II for the polymerization initiated with KPS (0.0075 w/w) or with AIBN (0.01 w/

Table I Copolymers' Composition, Obtained by PES, as a Function of Time for the Copolymerization of Styrene and Sodium Acrylate (ST/SAc = 90 : 10)

Time (min)	KPS 0.0075 w/w		AIBN 0.01 w/w	
	Sodium Acrylate	Styrene	Sodium Acrylate	Styrene
2	49.5	50.5	30.2	69.8
5	56.2	43.8	28.2	71.8
8	66.1	33.9	24.6	75.4
10	23.9	76.1	21.4	79.6
50	3.1	96.9	0.6	99.4

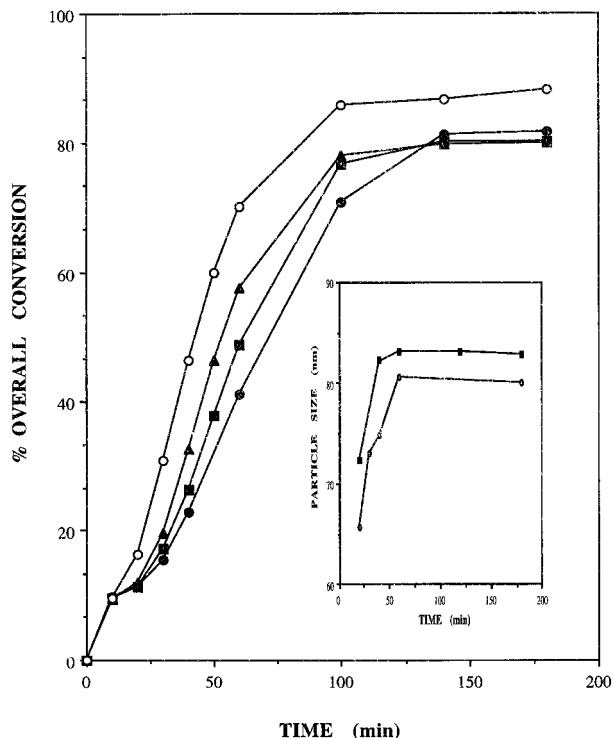


Figure 4 Overall conversion as a function of time for the emulsion polymerization of styrene and sodium acrylate (ST/SAc = 90 : 10) initiated at 60°C with different concentrations of AIBN: (●) 0.0015; (■) 0.0025; (▲) 0.005; (○) 0.010 in w/w monomers. Inset: Particle size as a function of reaction time for the reactions indicated with the same symbol.

w). With both initiators, molecular weights have values typical of emulsion polymerization, that is, on the order of millions.

IR spectra of poly(sodium acrylate), prepared by solution polymerization in water using KPS as initiator, and of polystyrene are shown in Figure 5. Poly(sodium acrylate) [Fig. 5(A)] exhibits a broad absorption band around 3400 cm^{-1} due to the stretching of the intermolecularly associated ONa (or OH) of the carboxylate group (probably

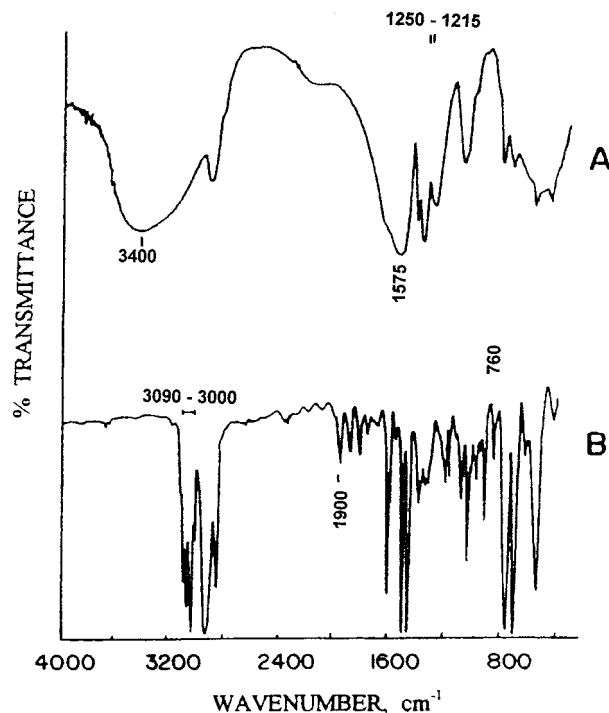


Figure 5 IR spectra of (A) poly(sodium acrylate) and (B) polystyrene.

through absorbed water molecules which cannot be eliminated by the drying treatment); it also exhibits a doublet at 1250 and 1215 cm^{-1} associated with the ether stretching of the carboxylate group. The C=O stretching band, which is typically observed around 1700 cm^{-1} in carboxylic compounds, appears as two bands at lower wavenumbers in poly(sodium acrylate) because of resonance of the COO^- group: a broad one at 1575 cm^{-1} due to the antisymmetric stretching and another at 1400 cm^{-1} due to the symmetric stretching. The spectrum of polystyrene [Fig. 5(B)] shows a triplet at 3090, 3060, and 3000 cm^{-1} that is related to C—H stretching and a region of overtones at $\sim 1900 \text{ cm}^{-1}$, which is typical of mono-

Table II Average Molecular Weights, Obtained by GPC, for the Copolymerization of Styrene and Sodium Acrylate as a Function of ST/SAc Ratio

ST/SAc	KPS 0.01 w/w		AIBN 0.01 w/w	
	$M_w \times 10^{-6}$	$M_n \times 10^{-6}$	$M_w \times 10^{-6}$	$M_n \times 10^{-6}$
70 : 30	2.90	2.3		
80 : 20			1.6	1.4
85 : 15			1.8	1.5
90 : 10	2.5	2.0	1.7	1.5

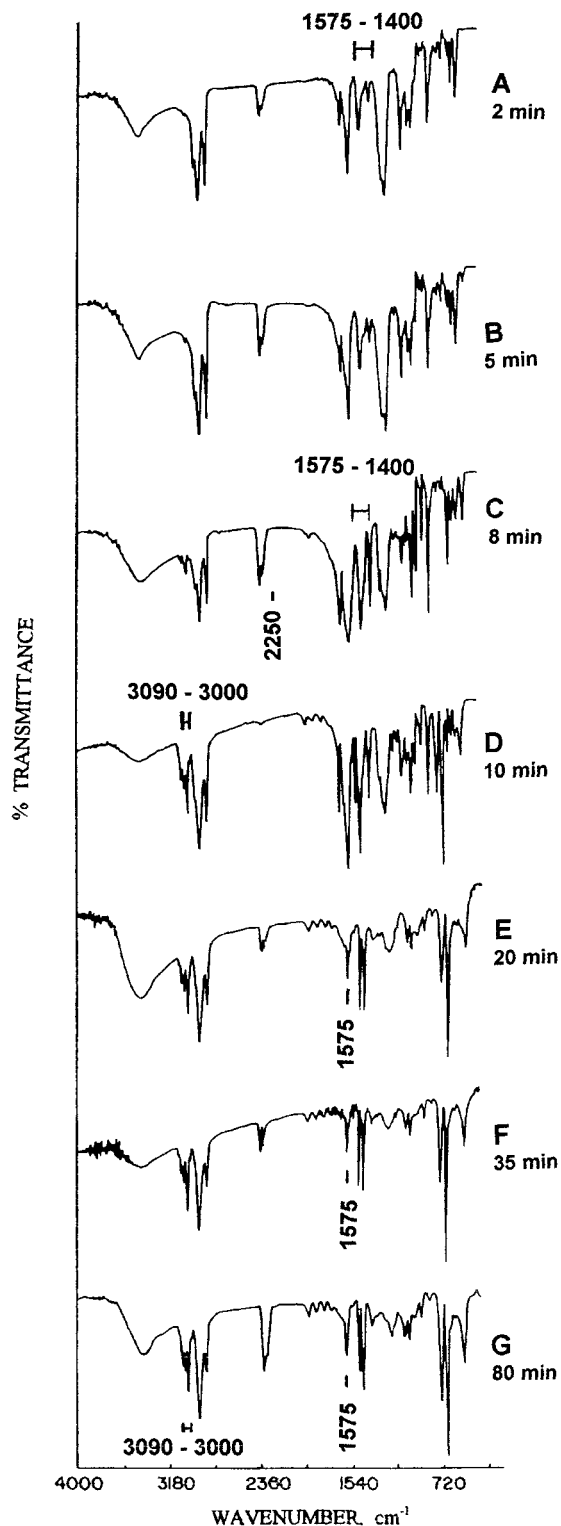


Figure 6 IR spectra of copolymers taken at different reaction times for the emulsion polymerization of styrene and sodium acrylate (ST/SAc = 90 : 10) initiated at 60°C with potassium persulfate (0.001 w/w monomers).

substituted aromatic compounds. Moreover, there is a sharp peak at 1600 cm^{-1} due to C=C stretching of the aromatic ring, and another one around 760 cm^{-1} due to C—H flexion.

IR spectra of samples taken at different times during the polymerization of styrene and sodium acrylate (in a ratio of 90 : 10) initiated at 60°C with KPS are shown in Figure 6. In spectra taken at 2, 5, and 8 min of reaction, strong bands associated with SAc are observed whereas bands due to polystyrene are weak or undetectable. In fact, the bands at 1575 and 1400 cm^{-1} of the carboxylate group appear intense and narrow in the spectrum of samples taken after 2 min. of reaction [Fig. 6(A)]. These bands increase in intensity and become wider in spectra taken at 8 min [Fig. 6(C)]. However, in spectra taken at larger reaction times, the absorption bands typical of polystyrene become noticeable [Fig. 6(D)] and more intense as the reaction proceeds [Fig. 6(E–G)]. Notice in spectra taken between 20 and 80 min [Fig. 6(E–G)] the narrowing of the C=O band at 1575 cm^{-1} caused by the superposition of the 1600 cm^{-1} band of polystyrene, and the increase in intensity of the triplet at 3000 cm^{-1} and of the overtones at 1900 cm^{-1} . In the spectrum taken at the end of the reaction [Fig. 6(G)], the absorption bands related to polystyrene are stronger than those associated with SAc, suggesting a larger number of ST units in the backbone of the copolymer. Incidentally, the doublet that appears at $\sim 2250 \text{ cm}^{-1}$ in all spectra is due to atmospheric CO_2 .

Figure 7 depicts IR spectra of samples taken at different reaction times when the polymerization (ST/SAc = 90 : 10) is initiated with AIBN. Again, at short reaction times, the bands associated with SAc are clearly visible in spectra [Fig. 7(A–C)], indicating that the copolymer contains large amounts of this monomer. However, a very weak triplet due to ST is observed in the region around 3000 cm^{-1} (which is not seen in spectra of samples taken at early times of the reaction initiated with KPS), demonstrating that the initiation mechanism with AIBN is different from that with KPS. In spectra taken at 5 min [Fig. 7(B)], the band of the carboxylic group becomes less intense, but the bands of the C=O and ONa (or OH) groups remain intense; at the same time, the intensity of the polystyrene triplet increases. In the spectrum at 8 min [Fig. 7(C)], the band of the carboxylate group becomes even less intense, whereas the triplet increases slightly in its intensity. In the spectrum of the sample taken at 10 min [Fig. 7(D)], two overtones at $\sim 1980 \text{ cm}^{-1}$ and the

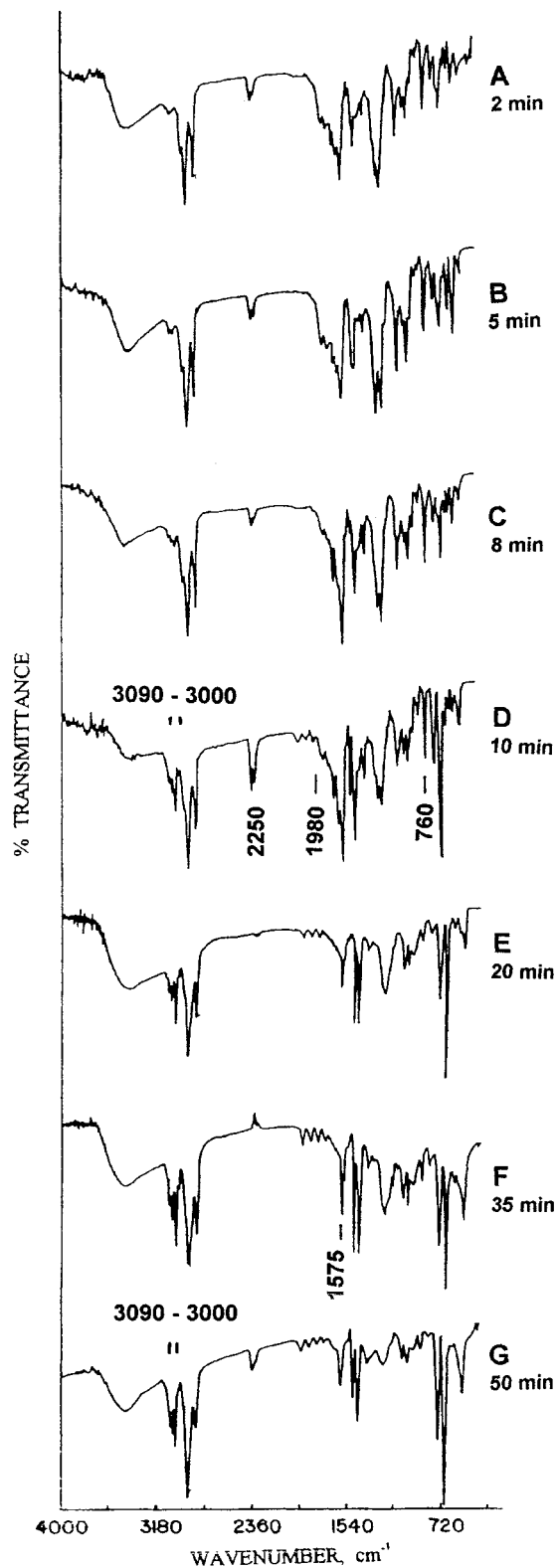


Figure 7 IR spectra of copolymers taken at different reaction times for the emulsion polymerization of styrene and sodium acrylate (ST/SAC = 90 : 10) initiated at 60°C with AIBN (0.0075 w/w monomers).

band at 760 cm^{-1} associated with styrene's C—H flexing appear. All this is caused by an increase in ST content in the samples with reaction time. Again, and similar to spectra of samples obtained with KPS, at the final stages of reaction, the spectra contain bands due to both poly(sodium acrylate) and polystyrene, confirming the formation of the copolymer, with a predominance of the ST bands, which indicates that the composition of the copolymer is richer in this monomer.

Figure 8 shows TMA thermograms, in compression mode, of polystyrene and of poly(sodium acrylate). For polystyrene [Fig. 8(A)], an inflection is detected around 100.1°C , which can be associated with the glass transition temperature (T_g) of this material.¹⁸ This transition can be detected more clearly by taking the derivative of the raw data (dashed line in Fig. 8). For poly(sodium acrylate), no thermal transition is observed from -100°C to $\sim 300^\circ\text{C}$. At 356°C , a minimum in the derivative is detected [Fig. 8(B)], which could be associated with the T_g of this polymer (which has not been reported in the literature). However, a simple inspection of the sample after the test (sample appears softer and brown) suggests that this transition may be due to the softening temperature of poly(sodium acrylate) and *not* to its T_g . At even higher temperatures (390°C), another transition is detected, which is not reversible, suggesting that this transition is probably caused by the degradation of the polymer by the rupture of C—C and C—H bonds. The absence of a glass transition temperature in poly(sodium acrylate) may be due to the rigidity of this material caused by the strong interactions among the charged carboxylate groups.^{4,6,7} Fitzgerald and Nielsen⁶ reported that partial ionization of poly(acrylic acid) with NaOH produces a twofold increase in the modulus and a notable increase in the glass transition temperature of the material. However, they neither reported the degree of ionization reached nor the measured values of the T_g .

Figure 9 shows thermograms, in compression mode, of samples prepared with a ratio of ST/SAC of 80 : 20 and KPS taken at different reaction times. The polymer sampled at early reaction times [Fig. 9(A)] exhibits two peaks in the derivative of the signal, a small broad one at 100°C , and a sharp one at 165°C . The sample taken at longer reaction times [Fig. 9(B)] shows again two transitions, a large broad peak at 100°C and a small peak at 135°C . Inasmuch as the samples used for the TMA test were washed with *n*-methanol and hot water, which are good solvents for poly-

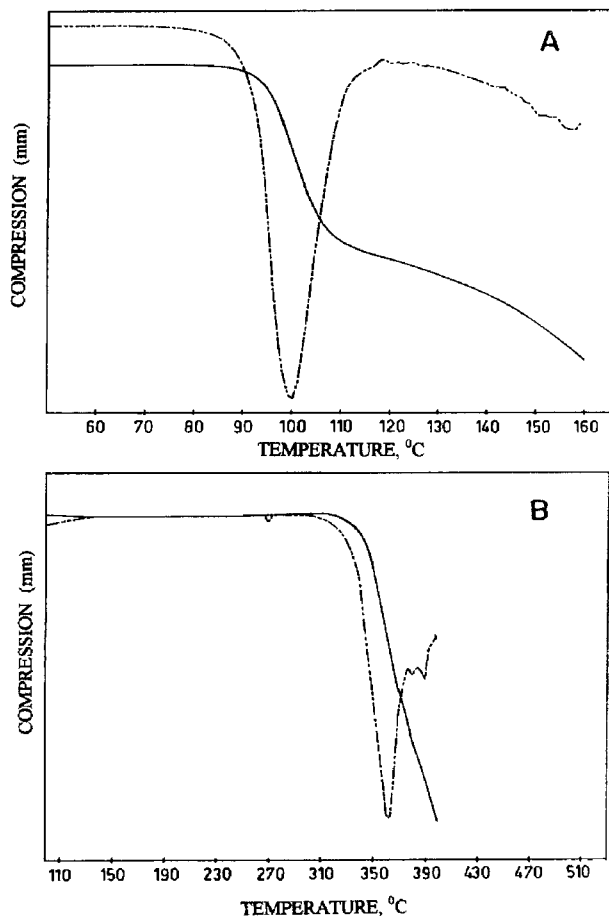


Figure 8 TMA thermograms in compression mode for (A) polystyrene and (B) poly(sodium acrylate).

(sodium acrylate) and SAc, and with THF, which is a good solvent for polystyrene, they cannot be physical blends of the homopolymers. Hence, the thermograms reveal features of the copolymer structure. The invariant transition detected at 100°C is undoubtedly related to the T_g of polystyrene blocky segments in the copolymer backbone. The transition detected at higher temperatures that shifts to lower temperatures as reaction time increases, may be associated with segments containing SAc and ST units. The shift in temperatures observed at different stages of reaction is probably caused by changes in composition of such segments.

Figure 10 depicts thermograms of samples taken at different reaction times during the emulsion polymerization of ST and SAc (ST/SAc = 80 : 20) initiated with AIBN. The thermograms again show two transitions, one at 100°C, which is invariant, and another one at higher temperatures, which moves to lower values as the reaction pro-

ceeds. Again, the invariant transition at 100°C is due to the T_g of polystyrene blocky segments of the copolymer, whereas the higher temperature transition may be associated with the T_g of segments composed of randomly arranged units of ST and SAc, whose composition varies with reaction time.

DISCUSSION AND CONCLUSIONS

Poly(styrene-*co*-sodium acrylate) has been synthesized by emulsion polymerization with a water-soluble (KPS) or an oil-soluble (AIBN) initiator. With both initiators, reaction rates are fast and final conversions are high (Figs. 1 and 2). However, KPS yields higher conversions with faster reaction rates. The final latices are opaque

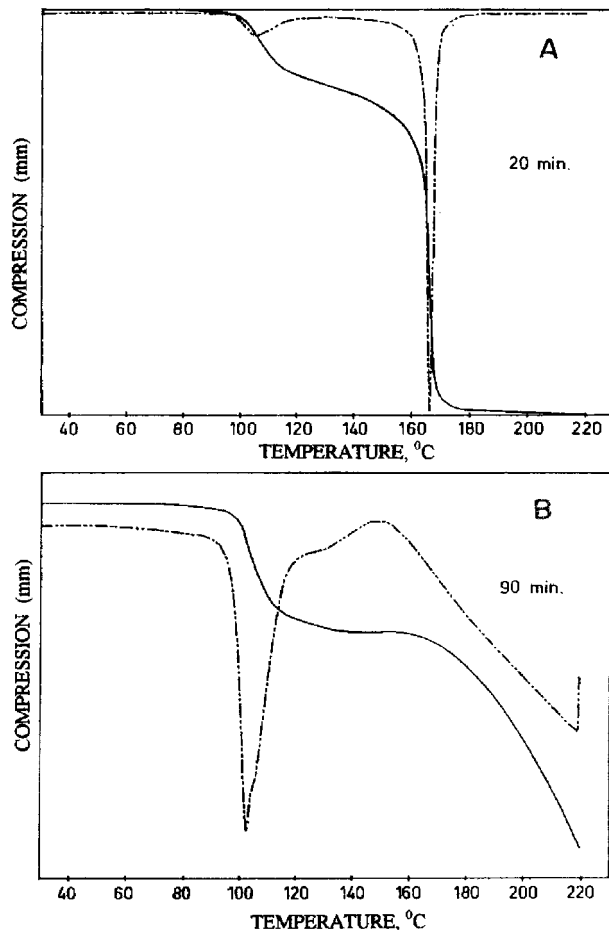


Figure 9 TMA thermograms in compression mode of samples taken at different times during the polymerization of styrene and sodium acrylate (ST/SAc = 80 : 20) initiated at 60°C with potassium persulfate (0.01 w/w monomers).

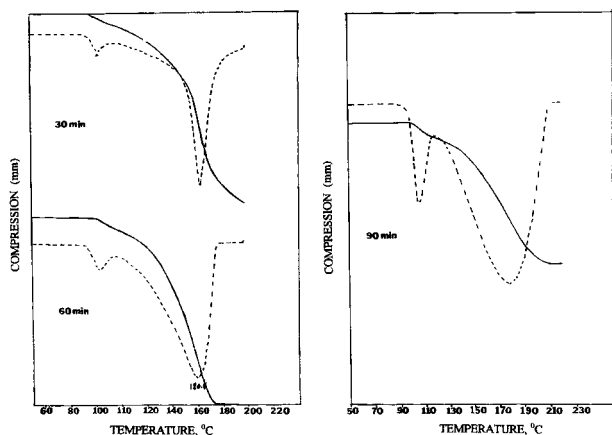


Figure 10 TMA thermograms in compression mode of samples taken at different times during the polymerization of styrene and sodium acrylate (ST/SAC = 80 : 20) initiated at 60°C with AIBN (0.0075 w/w monomers).

and have remained stable against coagulation for months. Latex particles are spherical with diameters ~ 70 – 80 nm, depending on the level and type of initiator concentration. The molecular weights of the final products are high ($>10^6$) (Table II).

Copolymer formation with both initiators was corroborated by FTIR spectroscopy, PES and SEM compositional measurements, and solubility tests. The IR spectra of the products obtained with KPS (Fig. 6) and with AIBN (Fig. 7) show absorption bands characteristic of both ST and SAC (Fig. 5). Inasmuch as the products were washed exhaustively with methanol, hot water, and toluene to remove any homopolymers that may have formed during the reaction, and the fact that the products were insoluble in methanol, which is a good solvent for poly(sodium acrylate), and only slightly soluble in THF, which is a good solvent for polystyrene, demonstrate that the spectra shown in Figures 6 and 7 do not correspond to physical blends of homopolymers. Moreover, the final products dissolve in 1,4-dioxane, which is *not* a good solvent for either of the homopolymers.

PES also reveals small amounts of sodium in the final samples (Table I). Even if the samples for PES were not dialyzed to remove some of the adsorbed surfactant (sodium dodecylsulfate), the amount of sodium in the products cannot be accounted for by the surfactant alone. Nevertheless, the concentration of SAC in the final copolymers is lower than the amount of SAC loaded in the reacting emulsion. The presence of sodium in the final samples was also detected by an X-ray detec-

tor in SEM. However, with this technique it was not possible to quantify sodium content.

The effects on reaction kinetics of the initiator concentration and of the ST/SAC initial ratio were also examined. Reaction rate increases as the concentration of initiator increases with both KPS (Fig. 3) and AIBN (Fig. 4). This is expected, regardless of the type of initiation mechanism (micellar or homogeneous), because an increase in initiator concentration should result in an increase in the flux of free radicals, and hence, in a higher probability of particle generation. This should result in faster reaction rates and smaller particle size in the final latex (insets in Figs. 3 and 4).

Reaction rate also increases with increasing concentration of SAC, that is, with decreasing ST/SAC ratio, for both KPS and AIBN (Figs. 1 and 2). Inasmuch as the concentration of ST in the aqueous phase is limited to its solubility limit¹⁹ and SAC is very soluble in water, the kinetic results strongly suggest that initiation is taking place mainly in the aqueous phase with both KPS and AIBN. However, there are important differences in polymer composition along the reaction with KPS and AIBN (Figs. 6 and 7). In fact, copolymers produced with KPS contain larger concentrations of SAC than those obtained with AIBN throughout the reaction (Table I). Hence, the mechanism of reaction appears to depend on the type of initiator used.

In conventional (ideal) batch emulsion copolymerization of water-insoluble monomers, reaction mechanism and copolymer structure depend mainly on the initial concentrations and reactivities of the participating monomers and it is fairly independent on whether a water-soluble or an oil-soluble initiator is employed.^{19,20} However, for the copolymerization of a polar monomer and a non-ionic monomer, the local concentration (partitioning) of the monomers is also important.^{21,22}

Previously we reported on the copolymerization of styrene with the water-soluble monomer acrylic acid and found that the water-soluble monomer reacted almost exclusively at early stages of the reaction, forming particles which acted as seeds where the comonomer was incorporated for most of the reaction.²² Then, at the final stages of the reaction, acrylic acid reacted again to produce homopolymer, that is, it was not incorporated into the backbone of the existing copolymer latex particles. Also, we reported in a short note on the polymerization of ST and SAC using KPS as initiator and showed by IR spectroscopy and rheometry

that poly(styrene-*co*-sodium acrylate) formed and that the incorporation of SAc into the copolymer was limited, regardless of the initial amount of SAc loaded into the system.²³ We calculated the reactivities of ST and SAc with the Q - e scheme.¹⁹ The Alfrey-Price equations are

$$\ln r_1 = \ln(Q_1/Q_2) - e_1(e_1 - e_2) \ln r_1 r_2 \\ = -(e_1 - e_2)^2$$

For ST, $Q = 1.00$ and $e = -0.80$, and for SAc, $Q = 0.71$ and $e = -0.12$.¹⁸ The calculated reactivities are 0.817 for ST and 0.77 for SAc. Hence, we concluded elsewhere that the reaction mechanism with the water-soluble initiator, KPS, must be controlled by the local concentration of monomers and the initiation site, and not by the reactivities.²³

Here we find that the location of the initiator is also important in determining the controlling reaction mechanism. With a water-soluble initiator, such as KPS, nucleation should occur mainly in the aqueous phase (homogeneous nucleation) where the concentration of SAc is much larger than that of ST. Hence, in the aqueous phase, SAc will react almost exclusively to form oligomeric radicals which will grow by recruiting more SAc and, occasionally, dissolved ST. When the concentration of SAc has decreased substantially, ST will be incorporated in the reacting particles which become stabilized by the available surfactant.

With oil-soluble initiators, such as AIBN, decomposition to produce free radicals occurs mostly within the monomer-filled micelles. In this case several events can take place. One is when the pair of free radicals react with ST solubilized in micelles and because of the small size of the micelles, the two growing radicals can terminate each other to produce a dead polymer particle. However, the large molecular weights achieved with AIBN (Table II) rules out this mechanism. Another possibility is that the free radicals react with monomer in the micelles and then one (or both) are desorbed to the aqueous phase, where they can grow by recruiting dissolved SAc or ST. Hence, in the emulsion copolymerization of a polar monomer and a nonpolar monomer initiated with an oil-soluble initiator, both homogeneous and micellar nucleation can occur.

FTIR spectra (Figs. 6 and 7) and PES (Table I), as a function of reaction time, support this hypothesis. The copolymers produced with KPS contain a larger proportion of SAc than the ones

yielded with AIBN (Table I). Hence, homogeneous nucleation seems to dominate the initiation stage with KPS, whereas both micellar and homogeneous nucleations occur simultaneously with AIBN. The fact that *not all* the SAc loaded in the system is incorporated into the copolymer suggests that a homopolymer forms. In fact, the similar reactivities of the two monomers and the much higher concentration of SAc in the aqueous phase facilitate the formation of poly(sodium acrylate).

The structure revealed by TMA thermograms is consistent with this hypothesis. The invariant transition detected at $\sim 100^\circ\text{C}$ is most likely due to the T_g of the polystyrene blocky segments in the copolymer. On the other hand, the transition that appears at higher temperatures is probably related to the T_g of the segments composed of randomly alternated ST and SAc units. The displacement of this transition to lower temperatures as the reaction proceeds is due to the enrichment of such segments with ST units, since the T_g of poly(sodium acrylate) appears to be much higher than the one of polystyrene.

Because of their high ST content, and the strong interactions that the acrylate groups can have with polar groups of polystyrene-incompatible polymers such as nylon and PVC, we are exploring the possibility of using these ionic copolymers as compatibilizers in blends. Scanning electron microscopy studies reveal that the addition of up to 4 parts per 100 of the ST/SAc copolymer improves the properties of a styrene-nylon blend and decreases substantially the particle size of the dispersed phase (nylon).²⁴ A full report will be presented in a forthcoming publication.

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