Polymer Bulletin 30, 207–214 (1993)

Polymer Bulletin

Emulsion copolymerization of styrene and sodium acrylate

S. Nuño-Donlucas[1], A. I. Rhoton[1], S. Corona-Galvan[1], J. E. Puig[1],*, and E. W. Kaler[2]

[1]Facultad de Ciencias Químicas, Universidad de Guadalajara, Guadalajara, Jal. 44430, Mexico
[2]Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

SUMMARY

Poly(styrene-co-sodium acrylate) has been synthesized by emulsion polymerization of styrene and sodium acrylate at a ratio of 9:1 with the water-soluble initiator potassium persulfate. The reaction is fast, conversions are high, and the evolution of particle size follows the conversion curve. The final latex is stable and contains spherical particles 70 nm in diameter. The presence of the copolymer is confirmed by several methods including FTIR, and the copolymer evolves from rich in sodium acrylate to rich in styrene as the reaction proceeds.

INTRODUCTION

There is growing interest in polymers containing ionic groups (ionomers) because of the variety of properties and applications that result from the interactions among ions bound to organic macromolecules (1 - 5). These interactions, which can be tailored by changing the amount and location of ionic species in the polymer backbone, affect both the physical and rheological properties of the host polymers [6]. Ionomers can be thermoplastic elastomers, are well-tolerated biologically, and have been used as selectively permeable membranes and microencapsulation agents (1 - 10).

Ionomers are usually synthesized either by copolymerization of small amounts of a functional monomer with an olefinically unsaturated monomer, or by direct functionalization of a preformed polymer (6, 11, 12). For example, carboxylic ionomers typically are prepared by free-radical copolymerization of acrylic or methacrylic acid with ethylene, styrene, butadiene, or similar comonomers, followed by neutralization to the desired degree with metal hydroxides, acetates, or similar salts (11). To our knowledge, the direct emulsion copolymerization of styrene with sodium acrylate has not been documented.

Here we report the emulsification of styrene and sodium acrylate with sodium dodecylsulfate (SDS), followed by copolymerization to form poly(styrene-co-sodium acrylate) after initiation with water-soluble potassium persulfate. Initiation occurs mainly in the aqueous phase and not in the styrene-swollen micelles.

EXPERIMENTAL SECTION

Sodium acrylate (Polyscience) with a purity greater than 99% was used as received. Reagent grade styrene (Scientific Polymer Products) was passed through a DHR-4 column (SPP) to remove the inhibitor immediately before use. Sodium dodecylsulfate (Tokyo Kasei) with a purity greater than 99% was used as received (its critical micelle concentration in water, measured by surface tension and conductivity, was equal to the value reported in the literature (13)). Hydroquinone and potassium persulfate (KPS) were reagent grade from Productos Químicos Monterrey, and water was doubly distilled.

Emulsion copolymerization of styrene and sodium acrylate (in an initial weight ratio of 90/10) was carried out at 60°C in a 2-L glass reactor. The ratio of water to monomers was

---

*Corresponding author

10/1 and the concentration of SDS in the water was 18 mM. The reaction vessel was charged with water and surfactant and heated to 60°C with continuous agitation under N_2. Monomers were then added and the emulsion initiated with a concentrated KPS aqueous solution. The reacting mixture was continuously stirred and sparged with N_2. Samples were taken at different times during the reaction and quenched by cooling and adding a 0.05 M hydroquinone aqueous solution. Copolymer was isolated by evaporation of volatiles in a vacuum oven and washing the residue exhaustively with alternating hot water and toluene. With this procedure, any non-adsorbed surfactant or non-reacted sodium acrylate, as well as any poly(sodium acrylate) or polystyrene formed during the reaction were eliminated. The remaining insoluble material (the presumed copolymer of sodium acrylate and styrene) was dried and weighed for conversion calculations. The copolymer was then formed into a pellet with KBr and examined in a 5 ZDA Nicolet FTIR spectrophotometer.

Latex particle size was determined by quasielastic light scattering (QLS) with equipment previously described (14). Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $<\Gamma> = 2q^2D$ (where D is the diffusion coefficient and q $[= (4\pi n/\lambda_0) \sin(\theta/2)]$ is the magnitude of the scattering vector), and the variance, v $(= [<\Gamma^2> - <\Gamma>^2]/<\Gamma>^2)$, which is a measure of the width of the distribution of the decay rates. The magnitude of the scattering vector was varied by changing the scattering angle, θ, from 30° to 120°. Here n is the index of refraction and λ_0 (488 nm) is the wavelength of the light in vacuum. The measured diffusion coefficients were represented in terms of apparent radii using Stokes law and the assumption that the solvent has the viscosity of water. Latexes were diluted up to 1000 times before QLS measurements to minimize particle-particle interactions.

Glass transition temperatures were measured in a Rheometrics Dynamical Spectrometer RDS-II using a torsion bar geometry . Temperature was increased 10 °C/min. with one minute intervals to allow for stabilization of the sample. The deformation strain was 1% and the deformation frequency was 1 rad/s. Copolymer bars were made by heating the polymer in a hydraulic press.

The sodium content of the copolymers was measured with a FMA-03 Spectra Analytical Instruments Plasma Emission Spectrometer (PES). Samples were dialyzed to remove any adsorbed surfactant, dried, and then incinerated in nickel crucible. The ashes were dissolved in a 3% HCl aqueous solution and then loaded into the spectrometer.

RESULTS

Overall conversion to copolymer as a function of time for the polymerization of styrene (ST) and sodium acrylate (SA) initiated with KPS (0.75 w/w monomers) is shown in Figure 1. The reaction is fast and the conversion is high (89% in 40 min.). Polymerization of styrene under similar conditions and concentrations of initiator and emulsifier is slower and reaches a lower final conversion (15). The initial reacting emulsion was opaque (milky) and stable at all times during the reaction. The resulting latexes are opaque and have not coagulated for over a year.

Figure 1 also shows the evolution of particle size as a function of time for this reaction. Particles grow with time (and conversion) until most of the monomers have been consumed, then both particle size and conversion remain roughly constant. QLS measurements show the final latex particles to be monodisperse and spherical with diameters around 70 nm. The normalized intensity autocorrelation function of the dilute latexes decays as a single-exponential, the variances are small ($v \leq 0.05$), and the diffusion coefficients are independent of q.

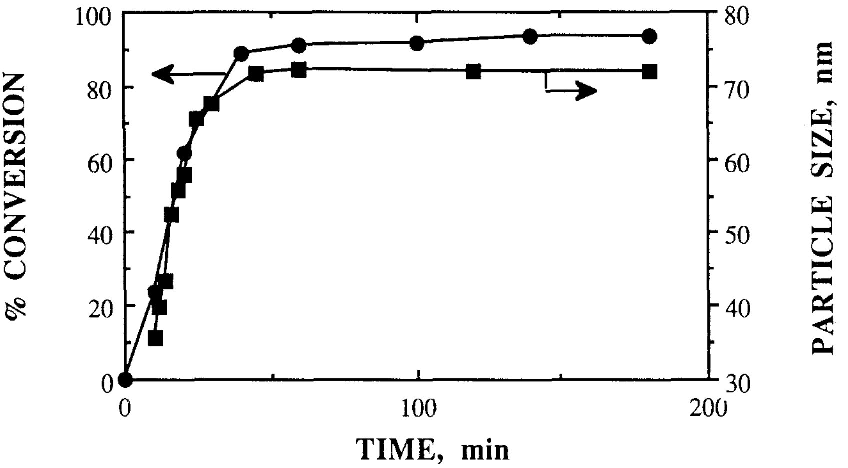

Figure 1. Conversion and particle size as a function of time for the emulsion polymerization of styrene and sodium acrylate (ST/SA = 90/10) using potassium persulfate (0.75 w/w monomers).

The IR spectrum of the final product (after washing with hot water and toluene) provides compositional information (Figure 2) and, for comparison, the spectra of both relevant homopolymers are shown in Figure 3. Poly(sodium acrylate) exhibits a broad absorption band around 3400 cm^{-1}, which is associated with the stretching of the intermolecularly associated O^- (or OH) of the carboxylate group (probably through absorbed water molecules), as well as a doublet at 1250 and 1215 cm^{-1} due to the ether stretching of the carboxylate group. The C=O stretching of carboxylic compounds, which is typically observed around 1700 cm^{-1} (16), appears for poly(sodium acrylate) at the lower wavenumbers of 1575 (broad) and 1400 cm^{-1} (due respectively to antisymmetric and symmetric stretching), because of resonance in the COO^- group (Figure 3).

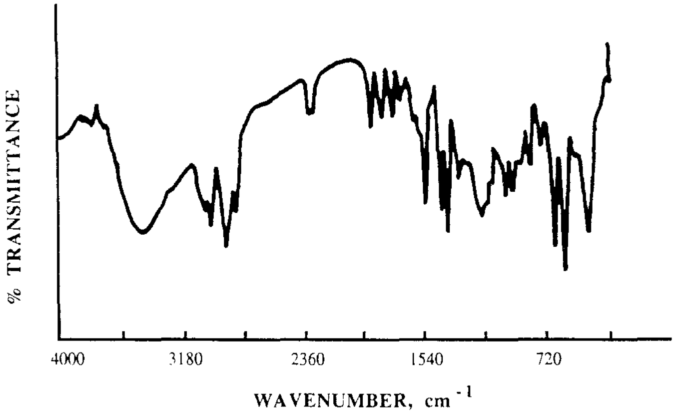

Figure 2. IR spectrum of copolymer synthesized by the emulsion polymerization of styrene and sodium acrylate (ST/SA = 90/10).

The spectrum of polystyrene (Figure 3) shows a triplet at 3090, 3060 and 3000 cm^{-1} that is related to C-H stretching, and a region of overtones around 1900 cm^{-1}. Both features are typical of monosubstituted aromatic compounds. In addition, 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 the stretching of C-H in styrene.

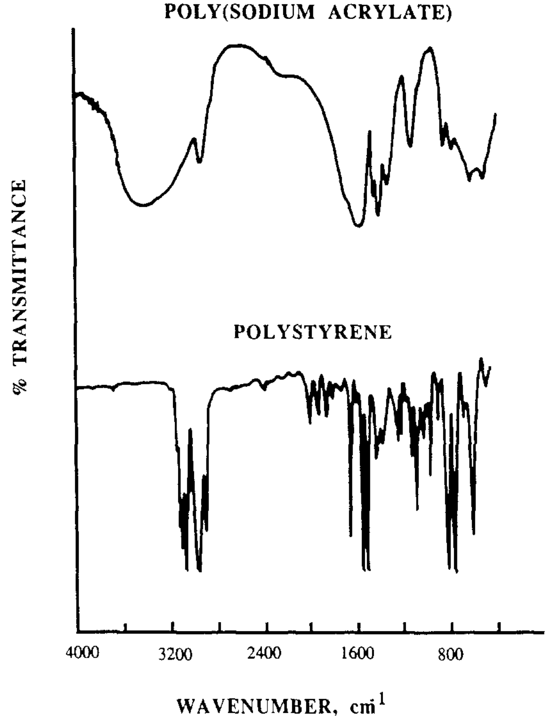

Figure 3. IR spectra of polysodium acrylate and polystyrene.

The spectrum in Figure 2 confirms the formation of the copolymer, i.e., in this spectrum there are absorption bands that are characteristic of both sodium acrylate and styrene, although the broad band due to antisymmetric stretching of the COO^- of sodium acrylate appears narrower in the copolymer because of superposition with the 1600 cm^{-1} band of the C=C groups of styrene.

The progress of the reaction was monitored by measuring the IR spectra of the copolymerization products (after washing with hot water and toluene) as a function of reaction time (Figure 4). Early in the reaction (Figure 4 at 10 min.), the spectrum of the product resembles that of poly(sodium acrylate) -- especially notice the broad band at 1575 cm^{-1} and the sharp band at 1400 cm^{-1} due to the COO^- group, and the broad band around 3400 cm^{-1} related to intermolecularly associated O^- group (with Na^+) of sodium acrylate (cf. Figure 3 and Figure 4 at 10 min.). As the reaction proceeds, absorption bands typical of styrene become stronger (notice in particular in spectra at 20 to 50 min. of Figure 4, the narrowing of the C=O band at 1575 cm^{-1} because of the growing superposition of the 1600 cm^{-1} band, and the increase in intensity of the triplet around 3000 cm^{-1} and of the overtones around 1900 cm^{-1}, both of which are related to styrene). In fact, the absorption bands from styrene structures are stronger than those from sodium acrylate in the spectrum of the sample at 50 min. (Figure 4), which suggests a predominance of styrene molecules in the backbone of the polymer.

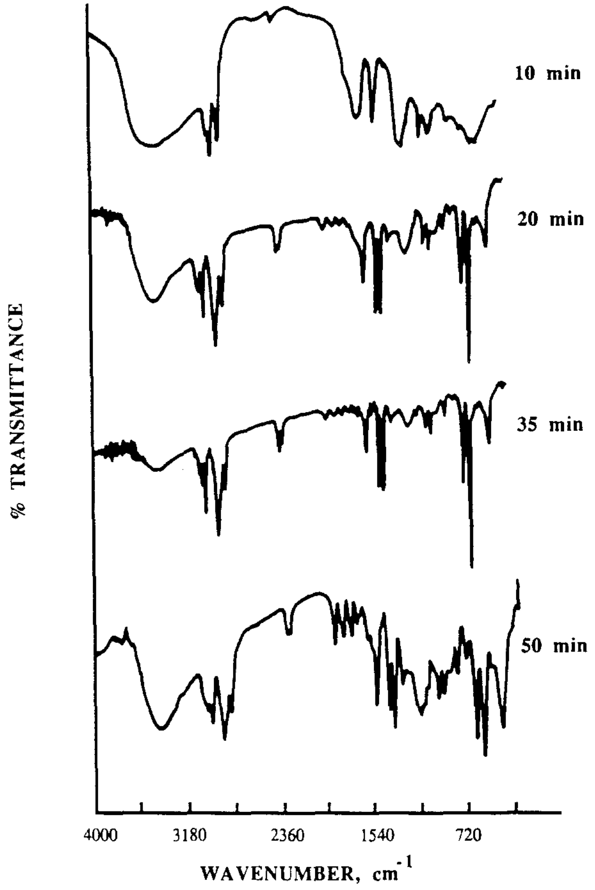

Figure 4. IR spectra of products of the emulsion polymerization of styrene and sodium acrylate (ST/SA = 90/10) as a function of reaction time.

The evolution of mechanical properties such as the viscous modulus (G") with reaction time is also consistent with the ultimate predominance of styrene in the polymer backbone. G" has been measured as a function of temperature T for the products of the polymerization of styrene and sodium acrylate after 10 and 50 minutes of reaction (Figure 5), with the latter sample chosen because the conversion has nearly reached its final value at this time. For comparison the G" (T) spectrum for polystyrene made by emulsion polymerization is also shown in Figure 5. The G" spectrum of the copolymer of styrene and sodium acrylate shifts to lower temperatures as conversion increases, and the spectrum after 50 minutes of reaction is closer to that of polystyrene than it is to that of the sample taken after 10 minutes of reaction.

To probe the reaction mechanism, the sodium content of the polymers was measured as function of conversion (Table 1). At short reaction times, the copolymer is rich in sodium acrylate (ca. 60 wt%), but as the reaction proceeds the sodium acrylate concentration drops and the final sample contains only 3 wt% sodium acrylate. Finally, we note that samples quenched after a short period of reaction (2 to 8 minutes) are insoluble in THF and toluene, which are good solvents for styrene, but the final copolymer is slightly soluble in THF (< 0.85 mg/mL), a result consistent with a higher content of styrene in the final product.

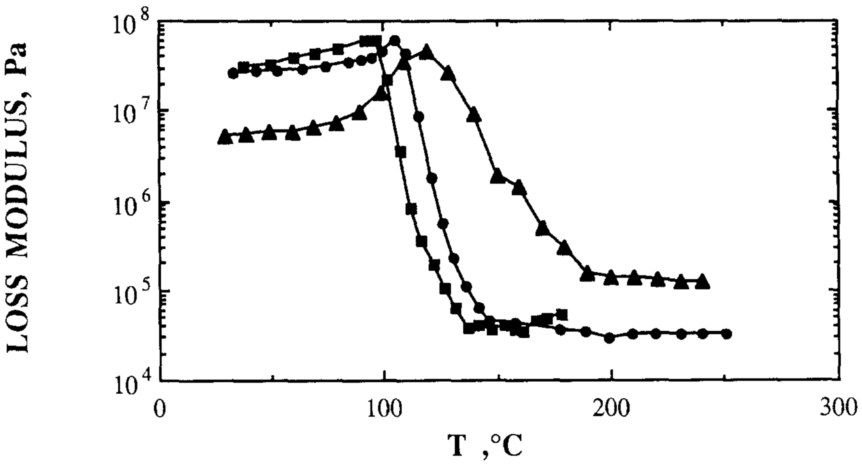

Figure 5. Loss modulus (G") vs time for styrene (■); and for products of the emulsion polymerization of styrene and sodium acrylate sampled at 10 min (▲) and 50 min (●).

Time of reaction min	Sodium acrylate wt%	Styrene wt%
2	49.5	50.5
5	56.2	43.8
8	66.1	33.9
10	23.9	76.1
50	3.1	96.9

Table 1. Copolymer composition determined by PES as a function of reaction time.

DISCUSSION AND CONCLUSIONS

Poly(styrene-co-sodium acrylate) has been synthesized by emulsion polymerization of styrene and sodium acrylate (ST/SA = 90/10) with a water soluble initiator, KPS. The reaction is fast, conversions are high, and the evolution of particle size follows the conversion curve (Figure 1). The final latex is opaque and has remained stable against coagulation for months. The latex particles are monodisperse and spherical with diameters of about 70 nm.

Copolymer formation was confirmed by FTIR, rheometry, PES compositional measurements and solubility tests. The IR spectrum of the product (Figure 2) exhibits absorption bands typical of both sodium acrylate and styrene (Figure 3). The material producing the spectrum in Figure 2 is *not* a physical blend of homopolymers because it is insoluble in methanol, which is a good solvent for poly(sodium acrylate), and is only slightly soluble in toluene or THF (good solvents for polystyrene). Moreover, the material examined by FTIR does dissolve in 1,4 dioxane, which is not a good solvent for either of the homopolymers.

The glass transition temperatures (T_g) of the samples taken at 10 and 50 minutes, as signaled by the sharp decrease in G" with temperature, are higher than the T_g of polystyrene (Figure 5). Poly(sodium acrylate) is ionic, so its T_g (which we could not detect by DSC) must be much higher than that of polystyrene. Thus the shift of the copolymer T_g to lower temperatures as the reaction proceeds is consistent with the PES compositional data (Table 1), which shows the copolymer formed at short reaction times to be richer in sodium acrylate than the copolymer formed later. There is evidence (17, 18) that the T_g of copolymers of either butadiene and sodium methacrylate or styrene and sodium methacrylate increases as the amount of the ionic monomer in the copolymer increases, in agreement with our results.

The IR spectra clearly show the product sampled at short reaction times to be quite similar to poly(sodium acrylate) (cf. Figure 3 and Figure 4 at 10 min.), although some weak bands due to styrene can be observed. As reaction takes place the absorption bands of styrene become more dominant, indicating that the number of styrene units in the polymer backbone increases with reaction time (spectra at 20 to 50 min. of Figure 4). In spite of the small content of sodium acrylate in the final copolymer, its properties (texture, appearance, toughness, solubility, etc.) are strikingly different from those of polystyrene.

To explain this kinetic behavior we calculated the reactivities of styrene and sodium acrylate using the Q-e scheme (19), since there is no experimental data for this system. The Alfrey-Price equations are

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

For styrene Q = 1.00 and e = - 0.80, and for sodium acrylate Q = 0.71 and e = - 0.12 (19), so the calculated reactivities are nearly equal: $r_{ST} = 0.817$ and $r_{SA} = 0.77$. Clearly the reaction mechanism should be controlled by the initial monomer concentrations and the initiation loci, and not by the reactivities. Hence, with a water-soluble initiator such as potassium persulfate, initiation should take place mainly in the aqueous phase where the concentration of sodium acrylate is much higher than that of styrene. In the aqueous phase, sodium acrylate will react first, and nearly exclusively, until its concentration decreases substantially and the oligomers formed in the aqueous phase reach a critical length and precipitate or perhaps migrate into styrene-swollen micelles. Once styrene is initiated, it will be incorporated preferentially because it is present in the emulsion overall at much higher concentration.

The results of a more detailed kinetic and rheological study in which the ratio of styrene and sodium acrylate are varied and the role of an oil-soluble initiator will be reported shortly.

ACKNOWLEDGMENT

We thank the Dirección de Vinculación y Transferencia de Tecnología de la Universidad de Guadalajara for assistance with the PES measurements. One of us (AIR) acknowledges the support of Industrias Resistol S.A., and we are grateful for the partial support of the National Science Foundation (INT-8996291).

REFERENCES

1. Holliday L (1975) Ionic Polymers, Applied Science Publ, London.
2. Einsenberg A, King M.(1977) Ion-Containing Polymers, Academic Press, New York.
3. Einsenberg A (1980) Ions in Polymers, Adv Chem Ser 187, American Chemical Society, Washington, DC.
4. Eisenberg A, Yaeger HJ (1982) Perfluorinated Ionomer Membranes, Am Chem Soc

Symp Ser 180, American Chemical Society, Washington, DC.
5. Wilson AD, Proser HJ (1983) Developments in Ionic Polymers-I, Applied Science Publ, London.
6. Weiss RA, MacKnight WJ, Lundberg RD, Mauritz KA, Thies C, Brant DA (1986) in Eisenberg A, Bailey FE (eds) Coulombic Interactions in Macromolecular Systems, ACS Symp Series 302, American Chemical Society, Washington, DC.
7. MacKnight WJ, Earnest, TR (1981) J Polym Sci Macromol Rev 16: 41 .
8. Bazuin CG, Eisenberg A (1981) Ind Eng Chem Prod Res Develop 20: 271.
9. MacKnight WJ, Lundberg RD (1984) Rub Chem Tech 57: 652.
10. Otocka EP (1971) J Macromol Sci Revs Macromol Chem C5: 275 .
11. Rees RW (1986) U.S. Patent 3,322,734, to E.I. Dupont de Nemours & Co.
12. Lundberg RD, Makowski HS, Westerman L (1980) in Eisenberg A (ed) Ions in Polymers, Adv Chem Ser 187, American Chemical Society, Washington, D.C.
13. Shinoda K, Nakagawa T, Tamamushi BI, Isemura T (1963) Colloidal Surfactants. Some Physicochemical Properties, Academic Press, New York.
14. Chang NJ (1986) Ph. D. Thesis, University of Washington.
15. Arce-Valenzuela AP (1991) M. Sc. Thesis, Universidad de Guadalajara, México.
16. Pouchert, CJ (1989) The Aldrich Library of FT-IR Spectra, Aldrich, Milwaukee.
17. Eisenberg A, Navratil M (1973) Macromolecules 6: 604 .
18. Eisenberg A, Navratil M (1974) Macromolecules 7: 84, 90.
19. Brandrup J, Immergut EH (1989) Polymer Handbook, John Wiley, New York.

Accepted December 11, 1992 K