Polymer Bulletin 31, 285–291 (1993)

Polymer Bulletin

Synthesis and characterization of copolymers of styrene and *N*-methylolacrylamide

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ABSTRACT

Copolymers of styrene (ST) and N-methylolacrylamide (NMA) were synthesized by emulsion polymerization for different initial weight ratios of ST/NMA. Fast reaction rates and high conversions are achieved regardless of the ST/NMA ratio. NMA content in copolymers, as deduced by DSC, FTIR and Kjeldhal analysis, is higher as the initial ST/NMA ratio decreases. Glass transition temperature of copolymers increases as the ST/NMA ratio decreases and it decreases with reaction time for a fixed ST/NMA ratio. The latter results and FTIR spectra as well as Kjeldhal analysis as a function of reaction time indicate that NMA reacts initially in the aqueous phase, after which ST, because of its overall larger concentration, is incorporated preferentially in the polymer.

INTRODUCTION

Functional monomers are being used in an increasing number of processes to modify and improve physical and processing properties of conventional polymers [1- 3]. Functional monomers are usually quite soluble in the aqueous phase. Hence the functionalization of water-insoluble monomers by emulsion polymerization becomes complicated by the distribution of monomers, reactivity ratios, emulsifier and initiator type, etc. [4 - 6]. One of these functional monomers is N-methylolacrylamide (NMA). When NMA is polymerized with styrene or acrylic monomers, it retains the methylol group which can undergo self condensation and crosslinking reactions [3]. Very few basic studies on the emulsion copolymerization of NMA with ST and acrylic monomers have been reported [8 - 11]. In particular, it has been documented that copolymer composition depends on monomers/water ratio, nature and amount of emulsifier, water solubility of the comonomer, etc. [8].

Here we report the emulsion polymerization of ST and NMA initiated with potassium persulfate as a function of the initial monomers ratio. The emulsifier was sodium dodecylsulfate. Copolymer formation was confirmed by FTIR spectroscopy, DSC and Kjeldhal analysis. Our results indicate that the kinetics are very similar to those of very hydrophilic monomers reacting with hydrophobic comonomers [6-11], that is, the hydrophilic monomer reacts preferentially at the beginning and at the end of the reaction, whereas the hydrophobic monomer reacts during the intermediate stage.

EXPERIMENTAL SECTION

Reagent grade ST (Scientific Polymer Products) was passed through a DTR-7 column (SPP) to remove inhibitor. NMA aqueous solution (60 wt%) from Cyanamid was

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used as received. Doubly distilled water was used. Sodium with a purity of 99% was from Tokyo Kasei. Hydroquinone and potassium persulfate were reagent grade from Aldrich. The solvents used were reagent grade from Aldrich or Merck.

Polymerization was carried out at 60 °C in a 1 L glass reactor with continuous agitation under a N_2 atmosphere. Monomers-to-water ratio was 1/10. The concentrations of sodium dodecylsulfate and potassium persulfate in the aqueous phase were 16 and 1.7 mM, respectively. Conversion was determined by evaporation in a vacuum oven or by precipitation with methanol. Samples were washed with hot water to remove excess surfactant and unreacted NMA, and then with N, N-dimethylformamide and toluene to remove any polyNMA or polyST that may have formed during the reaction.

Dried copolymers were examined by a 5ZDA FTIR Nicolet spectrometer. Glass transition temperatures were measured in a Perkin Elmer DSC 7 differential scanning calorimeter. NMA content in copolymers was also measured by the Kjeldhal method [12]. Particle size was measured with a Malvern 4700 QLS apparatus. Samples for QLS measurements were diluted 1000 times with water to prevent interparticle interactions.

RESULTS AND DISCUSSION

Figure 1 shows conversion vs. time for the copolymerization of ST and NMA as a function of initial monomers ratio. Reaction rates are fast (more than 80% conversion in 30 min.) and increase as the ST/NMA ratio decreases. In fact, the polymerization of ST under similar conditions is slower [Fig. 1]. Conversions are high (> 90%) and also increase as the ST/NMA ratio decreases. These results suggest that initiation takes place mainly in the aqueous phase where NMA, being in higher concentration than ST, can react with the SO_4^- to form oligomeric particles. These particles can then grow by recruiting more NMA from the aqueous phase and ST from the emulsified droplets.

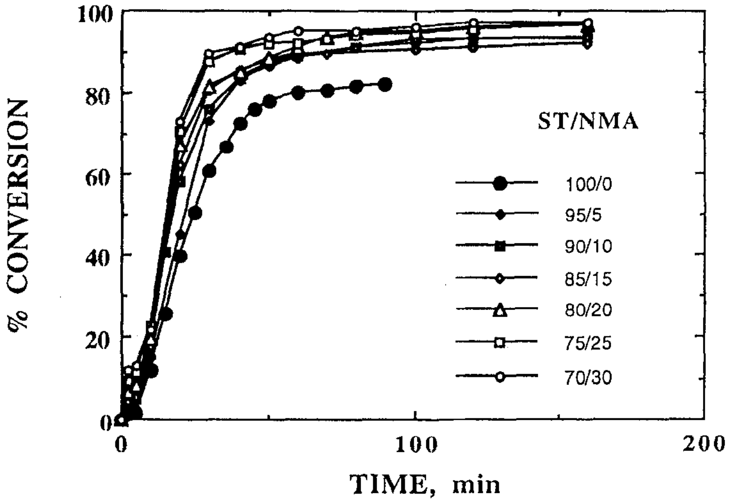

Figure 1. Emulsion polymerization of styrene and NMA as a function of ST/NMA.

Reacting emulsions were stable at all reaction times for all ST/NMA ratios. Final latexes are opaque and they remained stable for months. Figure 2 shows the evolution of particle size for ST/NMA equal to 95/05 and 70/30. Particle size is smaller at all reaction times for ST/NMA = 70/30 because there are more particles produced during initiation. This explains why the reaction rate is faster with the higher initial NMA concentration (Fig. 1). Again, this result suggests that initiation is occurring in the aqueous phase where the NMA is more likely to react because of its higher concentration.

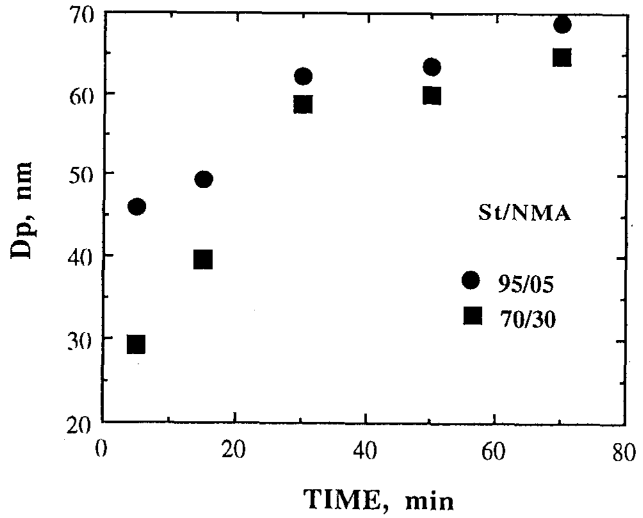

Figure 2. Particle size as a function of reaction time for St/NMA ratio of 95/05 and 70/30.

Copolymer formation was confirmed by FTIR spectroscopy. Figure 3 presents spectra of samples prepared by emulsion polymerization using different ratios of ST/NMA. The spectrum of a physical blend of polyST and polyNMA (85/15 by weight) is also shown for comparison. PolyST displays bands at 3080, 2947 and 1540 cm^{-1} due to stretching of the aromatic C-H, methyl and aromatic C=C groups, respectively, and several overtones around 2000 - 1730 cm^{-1} typical of benzene derivatives (13). PolyNMA, in turn, exhibits a strong and broad band around 3400 cm^{-1} associated with the OH group, and sharp bands at 1650, 1242 and 1026 cm^{-1} due to C=O, C-N and C-H groups, respectively (13). The spectra of the samples synthesized have bands of both ST and NMA, confirming the formation of the copolymer. In addition, the bands associated with NMA increase in intensity compared to those due to ST (notice in particular the decrease in intensity of the ST overtones, and the increase in intensity of the C=O peak), as the initial ratio of ST/NMA decreases, i.e. as the amount of NMA in the feed increases. These results indicate that more NMA is incorporated in the copolymer as the initial amount of NMA in the polymerization is increased.

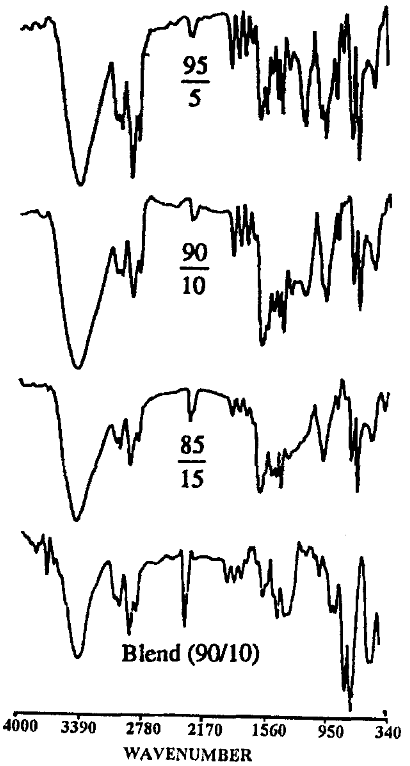

Figura 3. IR spectra of ST/NMA copolymers, prepared by emulsion polimerization, as a function of ST/NMA ratio. Spectrum of a physical blend of polystyrene and polyNMA in a weight ratio of 90/10 is also included.

Copolymer formation was also confirmed by DSC. Table 1 reports the glass transition temperature (T_g) of copolymers of ST/NMA as a function of the initial monomer ratio. The T_g of the samples increases as the ST/NMA ratio decreases, i.e. as the amount of NMA in the monomer feed increases. Inasmuch as the T_g of polyNMA (165 °C) (10) is greater than that of polyST (100 °C), these results indicate that the amount of NMA incorporated in the copolymers increases as the amount of NMA in the initial feed ratio (ST/NMA) decreases. Table 1 also reports the estimated composition of the ST/NMA copolymers using the measured T_g's and the equation of Woods (14), and the composition determined by the Kjeldhal method (12). Although the equation of Woods is very simple and not very reliable, the agreement of the calculated and the measured compositions is outstanding.

ST/NMA	T_g (°C)	ϕ_{NMA} (calc)	ϕ_{NMA} (exp)
95/5	103	0.046	0.041
90/10	104	0.061	0.060
85/15	106	0.092	0.084
70/30	107	0.108	0.101

Table 1. Glass transition temperatures of copolymers prepared using different initial ST/NMA ratios. ϕ_{NMA} (calc) is the fraction of NMA in the copolymer calculated by the Equation of Woods (14). ϕ_{NMA} (exp) is the measured fraction of NMA in the copolymer by the Kjeldhal method (12).

To test the hypothesis of homogeneous initiation and to understand the mechanism, FTIR and DSC measurements as well as Kjeldhal analysis were performed in copolymers sampled at different reaction times. Figure 4 shows spectra of samples taken at different times for the polymerization of ST/NMA (initial ratio of 85/15). The T_g's are reported in each spectrum.. The spectrum of the sample taken at 2 minutes of reaction (Fig. 4A) is quite similar to that of polyNMA. However, as the reaction proceeds, the spectra of the samples show absorption bands of both NMA and ST (Figs. 4B - 4D). In fact, absorption bands due to ST become more intense with reaction time. Concurrently, the T_g decreases as the reaction proceeds, and then increases slightly at the end of the reaction. Moreover, the NMA content as determined by the Kjeldhal method shows that the concentration of NMA is very high initially and then it decreases steadily as the reaction proceeds (Table 2). Evidently, NMA reacts preferentially at the beginning, but then ST is mostly consumed during the intermediate part of the reaction. Also, the slight increase in T_g at the end of the reaction may indicate that more NMA is being incorporated in the copolymer.

In conclusion, the functionalization of polyST with NMA is feasible. The amount of NMA that can be incorporated into the copolymer is limited, although it increases asymptotically to a limiting value as the ratio of ST/NMA decreases (Table 1). In spite of the small NMA content, the copolymers are quite reactive. For instance, they crosslinked upon drying. Hence these materials may be useful as compatibilizating agents of blends such as Nylon and PVC. This work is underway at our University (15).

ACKNOWLEDGMENT

This work was supported by the Consejo Nacional de Ciencia y Tecnología de México (Grant CONACYT # 92E020). One of us (J.B.F.) acknowledges the support of Industrias Resistol S.A..

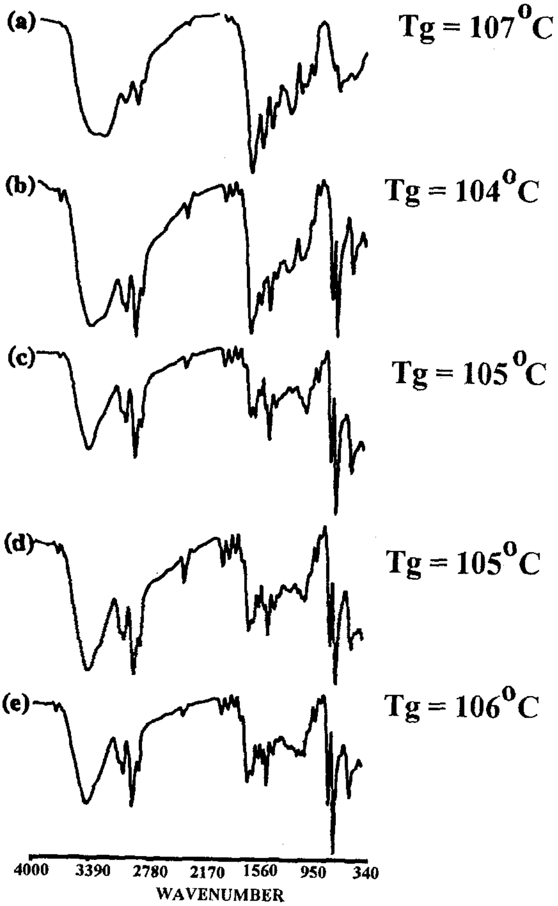

Figure 4. IR Spectra of samples taken at different reaction times for the polymerization of styrene and NMA: (a) 2 min.; (b) 5 min.; (c) 10 min.; (d) 30 min.; (e) 50 min.

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Accepted June 23, 1993 K