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SHORT COMMUNICATION

P. H. Wang
C.-Y. Pan

Emulsion copolymerization of styrene with acrylic or methacrylic acids – distribution of the carboxylic group

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P. H. Wang · C.-Y. Pan (✉)
Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei
Anhui 230026, China
e-mail: pcy@ustc.edu.cn

Abstract Studies on batch emulsion copolymeization of styrene with acrylic acid (AA) or methacrylic acid (MAA) were carried out. The effect of AA or MAA on the total conversion of the monomers was studied by a gravimetric method. The distribution of the carboxylic group in the copolymer microspheres was investigated by X-ray photoelectron spectroscopy and elemental analysis. The surface content of the carboxylic groups of styrene (St)/AA copolymer microspheres was found to be higher than that of St/MAA copolymer microspheres. The effects of partial neutralization of MAA in emulsifier-free emulsion copolymerization and seeded emulsion copolymerization on the distribution of the carboxylic group was also investigated.

Key words Carboxylic group · Copolymer microspheres · Partial neutralization

Introduction

Polymer microspheres (submicrometer) with various surface functional groups have extensive applications in the fields of biology, medical analysis, protein synthesis, chromatography, coatings and so on [1–5].

It is well known that emulsifier-free emulsion polymerization is widely used to prepare submicrometer polymer microspheres with various functional groups [6–10]. Generally, water-soluble monomers (functional monomers) employed in the emulsifier-free emulsion copolymerization system will be on the surface of the microspheres. Among these functional monomers, acrylic acid (AA) and methacrylic acid (MAA) have been extensively exploited to produce carboxylated polymer microspheres [11–14]. Such microspheres have been used in industrial areas, for example, as supports for the immobilization of fine metal particles, such as palladium and rhodium. These composite particles showed catalytic activity for some chemical reactions, such as hydrogenation [15]. When nickel or cobalt were incorporated onto the surface of such polymer microspheres, they showed magnetic properties [16–18]. Undoubtedly, the properties of these microspheres are greatly dependent on the distribution of the carboxylic group in the micropsheres. Therefore, adequate understanding of the factors affecting the distribution of the carboxylic functionality appears very important and is a prerequisite for proper control of the carboxylic group in the microspheres, which is of evident significance both scientifically and industrially. Numerous studies have been reported in the literature concerning the emulsion copolymerization of styrene with carboxylic monomers such as AA and MAA [11–14]. Most of the work concentrated on kinetic aspects of the copolymerization with the objective of deducing the kinetic model. Comparatively, less work was toward investigating the distribution of carboxylic groups in the microspheres commonly by means of conductometric and/or potentiometric analyses [19, 20]. To our knowledge, direct examination of the carboxylic group by means of X-ray photoelectron spectroscopy (XPS) is rare. In this work, the distribution of the carboxylic group in styrene (St)/AA and St/MAA copolymer microspheres prepared by emulsifier-free emulsion copolymerization was studied by XPS measurements and elemental analysis. In addition, in order to monitor or adjust the distribution of the carboxylic group in St/MAA copolymer microspheres, the effects of partial neutralization of MAA and seeded emulsion copolymerization on the distribution of the carboxylic group in St/MAA microspheres were also investigated.

Experimental

Materials

St (chemical reagent grade, Shanghai Chemical Reagent Co.), AA (chemical reagent grade, Shanghai Chemical Reagent Co.) and MAA (chemical reagent grade, Shanghai Wu-Lian Chemical Plant) were purified by distillation under reduced pressure. Ammonium persulfate (APS, Shanghai Chemical Reagent No. 1 Plant) was of analytical grade and was used without further purification.

Preparation of St/AA and St/MAA copolymer microspheres

St/AA and St/MAA copolymer microspheres (samples A–D) were prepared by emulsifier-free emulsion copolymerization of St with AA or MAA using APS as initiator. The recipes of the copolymerization are listed in Table 1. In the preparation of sample D, a prescribed amount of aqueous NaOH solution (equivalent molar ratio of NaOH/MAA = 0.2) was added into the copolymerization system. The procedure of preparation is the same as that in a previous report [17]. Sample E (St/MAA) was prepared by seeded emulsion copolymerization of St and MAA. The seed particles were produced by emulsifier-free polymerization of St (2 g) in 180 ml water using APS (0.01 g) as initiator for 3 h at 70 °C and 0.5 h at 80 °C. Then, the remaining St (18 g), MAA (3 g) and APS (0.09 g) in 20 ml water were dropped in within 2.5 h, and then the reaction was continued for 5 h. All the polymerizations were carried out under nitrogen at 70 °C with mechanical stirring at 350 rpm. The copolymer microspheres were purified by centrifugation–dispersion in a water cycle at least three times.

Characterization

The conversion was calculated by a gravimetric method. At different intervals, a certain amount of emulsion solution was withdrawn and immediately mixed with a small amount of hydroquinone to terminate the polymerization. After weighing, the emulsion was then dried at 68 °C overnight (around 12 h) in an oven to constant weight. The solid content was then measured, by which the monomer conversion was obtained. Meanwhile, a part of the emulsion withdrawn at different intervals during the polymerization process in the case of sample A (St/AA microspheres) was dried at 50–55 °C for the study of the composition of the microspheres by Fourier transform (FT) IR spectroscopy. IR spectra were recorded on a VECTOR-22 IR spectrometer using a KBr pellet with 32 scans and 4 cm^{-1} resolution. The size and morphology of the copolymer microspheres were investigated by transmission electron microscopy (TEM) using a Hitachi-800 microscope. XPS measurements were conducted on an ESCALAB MarkII system with a residual pressure of 3×10^{-9} mbar. The analyzer was used in the constant resolution mode, at a pass energy of 20 eV. The slit width of the analyzer was 6 mm. A Mg Kα radiation source ($h\nu = 1253.6$ eV) was used with an overall energy resolution of 1.0 eV. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. For both XPS and elemental analysis, the latices after centrifugation were dried at 68 °C overnight and were then dried in vacuo at the same temperature for 24 h. The samples in powder form were then stored in a dessicator for subsequent analysis.

Results and discussion

Rate of polymerization

Emulsifier-free emulsion copolymerization has been extensively used to prepare polymer microspheres on the submicrometer scale. Generally, the hydrophilic monomer in the copolymerization system acts as an emulsifier and locates on the surface of the polymer microspheres. The polymerization kinetics are then mainly determined by the addition of hydrophilic monomers. The influence of AA, MAA and partial neutralization of MAA on the copolymerization rate is illustrated in Fig. 1. It should be noted that in the calculation of the total conversion for partial neutralization of MAA (sample D), the maximum deviation of the total monomer conversion caused by the unreacted neutralized MAA which could not be removed in the drying process, was around 3% in weight. It is evident in Fig. 1 that the St/MAA system had a higher polymerization rate and a higher total conversion of monomers than the St/AA system did. By comparing curve b with curve c in Fig. 1, it can be seen that partial neutralization of MAA (curve b) decreased the rate of polymerization at the initial stage of the copolymerization (0–1 h), which led to a lower total conversion of monomers. The results obtained here are similar to those reported in the literature [11, 13].

Generally, the function of the acid monomer is twofold [11]: to induce the formation of polymer particles, thereby increasing the polymerization rate,

Table 1 Conditions for the copolymerization of styrene (St) with acrylic acid (*AA*) or methacrylic acid (*MAA*). The copolymerization conditions were 70 °C, 7 h for samples A–D

Sample	St (g)	MAA (g)	AA (g)	Ammonium persulfate (g)	H_2O (ml)	Conversion (%)	D_n (nm)	D_w/D_n
A	20		3	0.1	200	89.1	330	1.0002
B	20	3		0.1	200	96.1	175	1.0001
C	20	3		0.064	200	95.2		
D[a]	20	3		0.1	200	90.3	227	1.0003
E[b]	20	3		0.1	200			

[a] MAA was partially neutralized by NaOH

[b] Sample E was prepared by seeded copolymerization

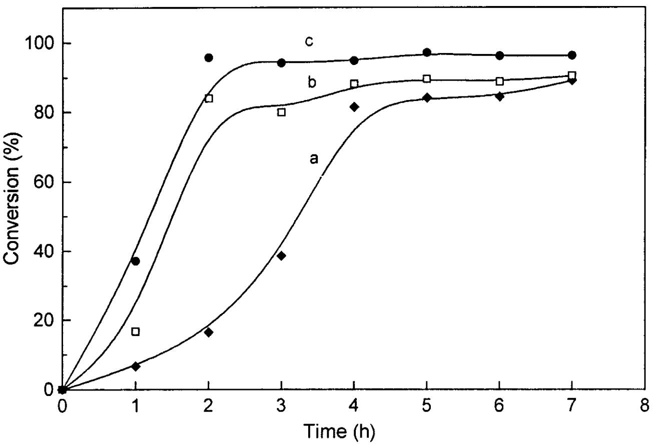

Fig. 1 Rates of copolymerization of Styrene (*St*) with acrylic acid (*AA*) (*a*), partially neutralized methacrylic acid (*MAA*) (b) and MAA (*c*). *a*, *b* and *c* correspond to samples A, D and B, respectively, in Table 1

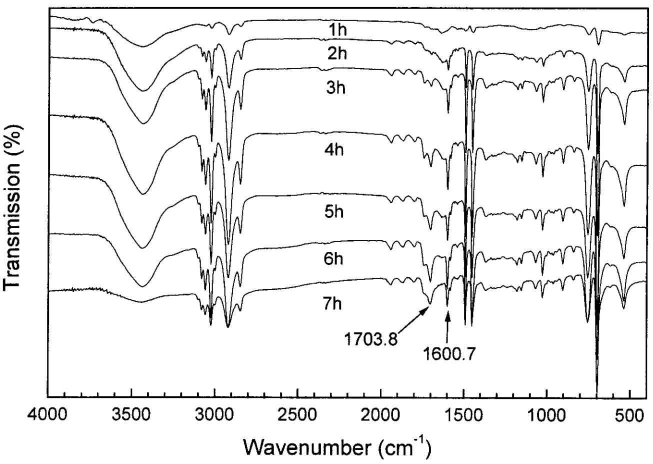

Fig. 2 IR spectra of the St/AA microspheres during the polymerization process (sample A)

and to stabilize the growing particles. Qualitatively, the ability of the acid monomer inducing particle formation can be explained by the theory of Fitch and Tsai [21]. Persulfate radicals induced polymerization of St and MAA (or AA) in the aqueous phase, the oligomers formed became insoluble, precipitated and agglomerated to form particles stabilized by the oligomer containing the carboxylic group. Particle growth continued by the polymerization of St and MAA (or AA) inside the particles. The particles were stabilized by the copolymers rich in MAA (or AA) located at the particle–water interface.

The progression of the composition of the copolymer microspheres during the copolymerization of St with AA (sample A) was studied by FTIR spectroscopy: the spectra are shown in Fig. 2. The spectra reveal well-defined bands of the St unit. The characteristic peak at 1704 cm^{-1} was attributed to carbonyl stretching of carboxyl groups, indicating the copolymerization of St with AA. Examination of Fig. 2 indicates that up to a polymerization time of 4 h the peak intensities at 1704 cm^{-1} are relatively weak, suggesting low AA content in the copolymer microspheres. From 4–6 h, the intensity of this peak increased significantly, indicating a significant increase in AA content in the copolymer microspheres. It appears that the polymerization time of 4 h was a “critical point” in the variation of the AA content in the copolymer microspheres. A reexamination of curve a in Fig. 1 reveals that the polymerization time of 4 h was also a “critical point” for total conversion, a threshold to the stage of “limiting conversion”, whereby the polymerization was controlled by monomer diffusion [22, 23]. On the basis of these observations, it is conceived that in the particle growth (or postnucleation) stage, a shift of the polymerization locus from the particle interior to the particle surface region occurred [24], i.e., from the end of the nucleation to the polymerization at 4 h, the polymerization of St was dominant and polymerization occurred mainly within the swollen St particles. In the subsequent period, the conversion of St was quite high and the polymerization of AA became relatively significant. The locus of such polymerization was considered to be at the particle surface region owing to its hydrophilicity.

As observed in Fig. 1, the polymerization rate in the St/MAA system was relatively higher than that of the St/AA system. On the basis of the homogeneous nucleation mechanism [21], the phenomenon can be simply explained as follows. MAA is more hydrophobic than AA. In the early stage of particle nucleation, the precipitation of St-*co*-MAA oligomers was easier than that of St-*co*-AA oligomers, i.e., occurred at relatively low molecular weight; therefore, more particles were formed in the case of copolymerization of St and MAA, i.e., the critical particle size in the St/MAA system was smaller than that in the St/AA system. In the stage of subsequent particle growth, the newly formed particles became rapidly swollen with St monomer. The number of hydrophilic monomers inside the particles depended on their hydrophobicity. The polymerization mainly occurred in the swollen St polymer particles as discussed previously. Therefore, the copolymerization rate or total conversion was, from some viewpoint, mainly determined by the polymerization or conversion of St. As we know, the more particles there are, the faster the polymerization rate; thus, the St/MAA system had a higher polymerization rate. This explanation is confirmed by Fig. 3, which shows the TEM photographs of the copolymer microspheres prepared from the St/AA and St/MAA systems. The particle sizes calculated on the basis of the photographs are listed in

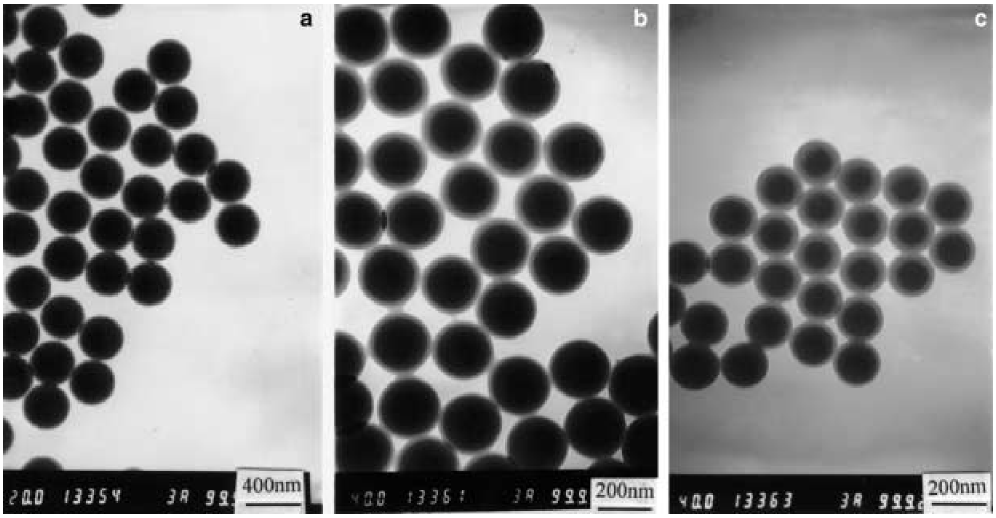

Fig. 3 Transmission electron microscope photographs of copolymer microspheres of styrene with **a** AA, **b** partially neutralized MAA and **c** MAA. **a**, **b** and **c** correspond to samples A, D and B, respectively, in Table 1

Table 1. As we expected, the particle size of the St/MAA microspheres is much smaller than that of the St/AA microspheres. For the same amount of monomer, the smaller the particles, the greater the number of particles, resulting in a higher rate of copolymerization as observed in Fig. 1.

Comparison of curve b with curve c in Fig. 1 shows that partial neutralization of MAA decreased the rate of copolymerization at the early stage of the copolymerization (0–1 h). The partial neutralization of MAA led to the decrease in the hydrophobicity of MAA. For the same reason as discussed earlier, this would result in a larger particle size as indicated in Fig. 3 and Table 1, and consequently the rate of polymerization decreased somewhat as observed in Fig. 1.

Distribution of carboxylic group

Direct examination of the distribution of the carboxylic group both on the surface and in all the microspheres of St/AA and St/MAA copolymer microspheres was carried out by XPS measurement and elemental analysis. A typical XPS full-scan spectrum (sample E) is given in Fig. 4. It can be seen that the main elements on the microsphere surface were carbon and oxygen (hydrogen cannot be detected by XPS). The C1*s* spectra of all the samples in Table 1 is shown in Fig. 5; they clearly show the presence of two types of carbons at binding energies of 284.8 and 289.2 eV, respectively. The former is attributed to the carbons in the C–C and C–H linkages, while the latter is attributed to the carbons in the carboxylic groups, i.e., –COOH groups. A typical O1*s* spectrum (sample E) in shown in Fig. 6 and is mainly composed of two peaks at 532.2 and 533.7 eV. These two peaks are attributed to the two oxygen atoms in the –COOH groups [24], respectively. These observations

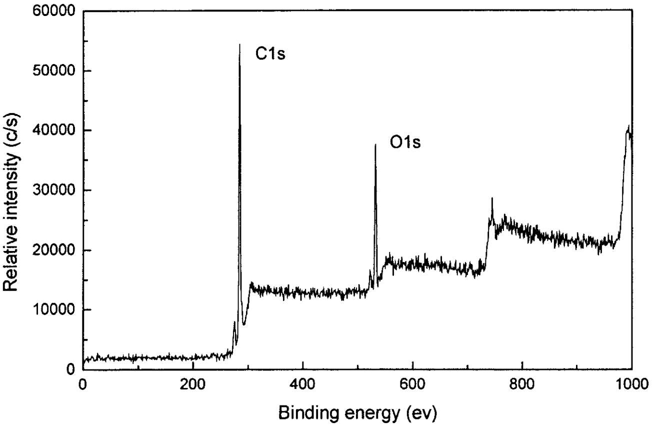

Fig. 4 The full-scan spectrum of St/MAA copolymer microspheres (sample E)

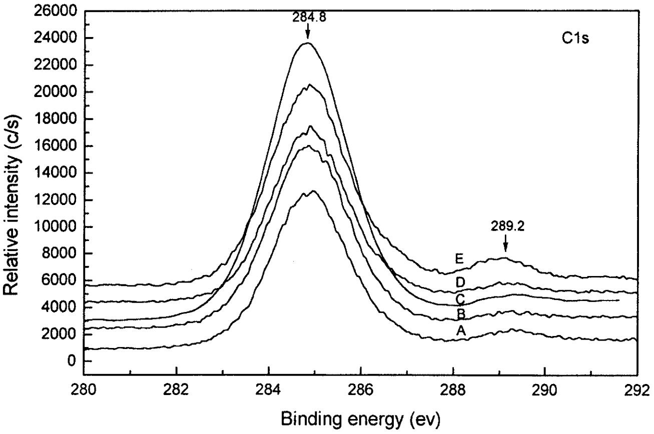

Fig. 5 C1*s* spectra of St/AA and St/MAA copolymer microspheres

proved the presence of carboxylic functional groups on the surface of both the St/AA and St/MAA copolymer microspheres.

The results of elemental analysis and surface XPS measurements are listed in Table 2. The ratio of C_{COOH}/C_{TOTAL} was calculated from the percentage of carbon at 289.2 eV against all the carbon atoms at 284.8 and 289.2 eV in Fig. 5, and is a direct indication of the distribution of the carboxylic group. By comparing the elemental analysis of the St/MAA microspheres, it was deduced that the St/AA microspheres had a lower oxygen content and lower C_{COOH}/C_{TOTAL} ratio (Table 2). However, from the XPS results in Table 2, the C_{COOH}/C_{TOTAL} ratio of the St/AA microspheres is larger than that of the St/MAA microspheres, indicating that the surface layer of the former contained more carboxylic groups than the latter. The probable reason is as follows. At the stage of particle growth, the newly formed particles were swollen by St monomer. Compared with hydrophilic AA monomer, the swollen particles contained more MAA monomer. When the copolymerization in the particles proceeded, relatively hydrophobic monomer MAA easily diffused into the particles, where it polymerized probably not only inside the particles but also at the surface layer of the particles. The oligomers containing MAA produced in the aqueous phase precipitated onto the surface of the particles and stabilized the growing particles. Comparatively, the relatively highly hydrophilic monomer AA tended to copolymerize either at the particle surface region or in the aqueous phase. During the emulsion copolymerization, less AA entered the particles owing to its hydrophilic nature. Even if AA monomers were present in the particles, most of them were probably copolymerized at the particle–water interface; therefore, at the same feed ratio, the St/MAA copolymer microspheres contained more MAA inside the particles, but less MAA on the particle surface compared with the St/AA microspheres as indicated in Table 2.

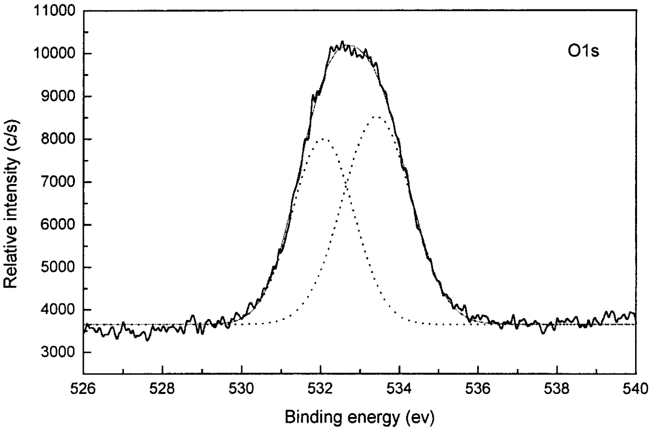

Fig. 6 O1*s* spectrum of St/MAA copolymer microspheres (sample E)

Table 2 Results of elemental and X-ray photoelectron spectroscopy (*XPS*) analyses

Sample	Elemental analysis				XPS
	C	O	O/C	C_{COOH}/C_{TOTAL}	C_{COOH}/C_{TOTAL}
A	90.02	1.72	0.0143	0.72	6.62
B					2.80
C	86.71	4.93	0.0430	2.15	2.63
D	87.41	4.60	0.0395	1.98	5.09
E	86.91	5.19	0.0448	2.24	8.32

In order to confirm further this explanation, MAA was partially neutralized by addition of NaOH into the copolymerization system. The results are listed in Table 2 (sample D). It can be found from Table 2 that partial neutralization of MAA led to a decrease in the oxygen content and the C_{COOH}/C_{TOTAL} ratio all the particles, but to an increase in the C_{COOH}/C_{TOTAL} surface ratio, i.e., in surface carboxylic groups. As discussed previously, partial neutralization decreased the hydrophobicity of MAA [13]. Thereafter, the concentration of MAA in the polymer particles decreased and more MAA tended to polymerize in the aqueous phase and at the particle–water interface. This inevitably led to more MAA on the surface and to less MAA in all the particles as shown in Table 2.

The effect of seeded emulsion copolymerization of MAA with St on the distribution of the carboxylic group was studied. The result is listed in Table 2. The surface layer of the St/MAA microspheres prepared by seeded emulsion copolymerization contained the highest level of carboxylic group (see E in Table 2). St is good solvent of polystyrene; therefore, it could swell the polystyrene seeds, whereby they might polymerize. This would cause a significant increase in the relative quantity of MAA in the aqueous phase compared with that without seeds. As a result, the surface of the microspheres obtained in the presence of seeds was rich in carboxylic groups.

Conclusions

In the batch emulsifier-free emulsion copolymerization of St with MAA or AA, the copolymerization rate of MAA with St was higher than that of AA with St. Partial neutralization of MAA led to a decrease in the polymerization rate.

The distribution of the carboxylic group was examined by XPS measurements and elemental analysis. The number of surface carboxylic groups of the St/AA copolymer microspheres was found to be much higher than that of the St/MAA copolymer microspheres.

Partial neutralization of MAA and seeded copolymerization significantly increased the number of carboxylic groups on the surface of the St/MAA copolymer microspheres.

The distribution of the carboxylic group can be controlled by selecting the proper hydrophilic monomers, adjusting the hydrophilicity of the monomers and using the correct polymerization method.

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