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Synthesis and Characterization of Acrylic-Itaconic Acid Copolymer Used as an Environmental Friendly Polycarboxylic Detergent Builder

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Itaconic acid-based copolymers used as detergent builders are synthesized and its builder performances are characterized and compared with sodium tripolyphosphate. The acrylic-itaconic acid copolymer (AA-Co-IA) exhibits better balance cleaning performance. The detergency, antisediment ability, dispersibility for calcium soap, buffering pH capacities of the AA-Co-IA are better, but the surface activity is lower in comparison with those of the acrylic acid-maleic anhydride copolymer (AA-Co-MA), the acrylic acid-itaconic acid-maleic anhydride copolymer (AA-Co-IA-Co-MA) and sodium tripolyphosphate. All the three copolymers have a good synergism with sodium dodecyl benzene sulfonate (LAS), so that their incorporation can lower the surface tension of the sodium dodecyl benzene sulfonate solution obviously. The biodegradability of the AA-Co-IA is obviously better than that of AA-Co-MA and AA-Co-IA-Co-MA. So, the AA-Co-IA is a promising green detergent builder with high biodegradability and good detergent performance.

Key Words: Acrylic-itaconic, Acid copolymer, Detergent performance, Copolymerization, Polycarbonates, Biodegradable.

INTRODUCTION

Builder is one of the two important ingredients in laundry detergent and plays a key role in washing processes[1]. For a long time, sodium tripolyphosphate (STPP) as a detergent builder with good performance has been widely used in detergent industry. Unfortunately, the discharges of large phosphorus-containing detergent wastewater causes water eutrophication of rivers and lakes and seriously destroys the ecological environment, which brings about the worsening of water quality and the huge death of aquatic organisms[2,3]. Therefore, many countries have issued the laws and regulations to ban or limit using sodium tripolyphosphate as a detergent builder since 1970s.[4,5] As a consequence, phosphate-free detergent is an inevitable trend for detergent industry and it has become a hot topic to developing nonphosphate detergent builders[6-8]. Many detergent phosphate replacements have been reported[9-13], among which the most promising varieties are mainly zeolite[14-18], sodium disilicate[19-25] and polycarboxylates[26-32].

Up to now, polycarboxylates studied widely as detergent builders are mainly polyacrylate (PAA) and acrylic acid-maleic anhydride copolymer salt (AA-Co-MA), which have many merits such as good detergency, resistance to hard water and nontoxicity, but their balance detergent property is inferior to sodium tripolyphosphate[1,4,33-35].

Many research results have revealed that the detergent effects of polycarboxylates are relevent to the content of carboxyl in the molecular chain. The higher content of carboxyl results in the greater charge density, the better chelating and the better dispersing capacity. Therefore, the detergent performance of polycarboxylates can be improved by copolymerization of acrylic acid with maleic anhydride which containing two carboxyl groups[8,33-35]. However, the polymerization activity and the copolymerization ability of maleic anhydride with acrylic acid are poor due to the symmetrical molecular structure of maleic anhydride with two electron-withdrawing carboxyl groups bonded respectively to the two double bond carbon atoms, which limits the quantity ratio of maleic anhydride in the copolymers and improvement of the detergent performance of AA-Co-MA. Itaconic acid (IA) also contains two carboxyl groups, but its polymerization activity and its copolymerization ability with acrylic acid are higher because of its asymmetrical molecular structure with one electron-withdrawing carboxyl group bonded to the double bond carbon atom through methylene group. Therefore, it is likely that detergent performance of AA-Co-IA is better than that of AA-Co-MA.

An even more important issue is that the biodegradability of polyacrylate and AA-Co-MA is poor,[1,29,36-37] with the consequence of accumulation in the environment for a long time leading to pollution. The utilization of renewable resources particularly the biologically produced materials has attracted increasing interest in the last decades[9,27,28,37-39]. Introducing biodegradable segments into the backbone of the synthetic polymer is an effective way to make the high biodegradable polymer builder[37]. Itaconic acid, which is produced by fermentation from renewable biomass resources, is one of these products and its polymer [poly(itaconic acid)] has better biodegradability[36,40] so poly(itaconic acid) and its copolymers used as detergent builders can be more environmental friendly. Itaconic acid based homo- and copolymers have been widely studied and its industrial applications in some areas have been found by many research groups[36,40-56] but there are few reports on its application in detergent industry[31,32,57].

For these reasons, we studied the synthesis and detergent performance of the AA-Co-IA and AA-Co-IA-Co-MA, then a comparative study of builder performance and biodegradability of AA-Co-IA, AA-Co-MA, AA-Co-IA-Co-MA and sodium tripolyphosphate is reported in this paper.s

EXPERIMENTAL

Itaconic acid (IA) was produced by Qingdao Langyatai Group. Acrylic acid (AA), maleic anhydride (MA), sodium tripolyphosphate (STPP), ammonium persulfate, sodium hydroxide, sodium carbonate, sodium silicate, sodium sulfate, carboxylmethylcellulose and sodium dodecyl benzenesulfonate (LAS) were all analytical reagents and purchased from Tianjin Kermel Chemical Reagent Co. Ltd. All materials were used as received.

In order to understand the copolymerization characteristics of acrylic acid, itaconic acid and maleic anhydride, the competitive polymerization ratios(r) were calculated using the Alfrey-Price Q-e equation[58].

Synthesis of AA-Co-IA: The AA-Co-IA was synthesized in the light of optimum conditions described in the literature[57]. The synthesis was performed in a four-neck 250 mL flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and two dropping funnels. The stirring rate was kept at 150 rpm throughout the synthesis. The reaction temperature was controlled using a thermostatted water bath. 10 g (0.077 mol) itaconic acid and 40 mL deionized water were taken into the flask and the contents was heated to 80 to 85 ºC under adequate stirring. 20 g (0.278 mol) acrylic acid monomer and 2 g ammonium persulfate dissolved in 15 mL deionized water were then added dropwise from separate dropping funnels into the reactor at a temperature of 80 to 85 ºC over a period of 2.5 h. After addition of all the ingredients, the reaction temperature of 80 to 85 ºC was maintained for an additional 3.5 h. Then, the contents were cooled to ambient temperature. Finally the copolymer solution was obtained by neutralizing the contents to pH = 7.5 to 8.0 with 1.5 mol/L of sodium hydroxide solution. The molar conversion of total monomers is 100 %. The solid content of the solution is 31.05 wt % and the intrinsic viscosity is 53.2 mL g^{-1}.

Synthesis of AA-Co-MA: The AA-Co-MA was synthesized in the light of optimum conditions described in the literature[59]. The synthetic procedure is the same as that of the AA-Co-IA except to replace 10 g itaconic acid (0.077 mol) with 7.55 g (0.077 mol) maleic anhydride. The molar conversion of total monomers is 90.92 %.The solid content of the solution is 30.06 wt % and the intrinsic viscosity is 50.4 mL g^{-1}.

Synthesis of AA-Co-IA-Co-MA: The synthetic procedure of AA-Co-IA-Co-MA is the same as that of the AA-Co-IA except to replace 3.25 g (0.025 mol) itaconic acid with 2.45 g (0.025 mol) maleic anhydride. The molar conversion of total monomers is 94.22 %. The solid content of the solution is 30.36 wt % and the intrinsic viscosity is 155.4 mL g^{-1}.

Analysis of the copolymer properties: The molar conversion of total monomers was determined by a bromination method[60]. The solid content of the copolymer solutions was determined gravimetrically.

Intrinsic viscosity of the copolymers was measured at 30 ± 1 ºC by an Ubbelohde viscometer (capillary inner diameter is 0.5-0.6 mm, Longgang glass meter plant in taixin) using deionized water as a solvent. Intrinsic viscosity[η] was calculated using the following equation:

$$[\eta] = \frac{\sqrt{2[(t - t_0)/t_0 - \ln(t/t_0)]}}{C}$$

where, C is the weight concentration of polymer solutions, g/mL; t_0 and t are the elution time (in sec) of deionized water and the solution respectively.

Determination of the detergent performance: The dispersing ability for calcium soap was measured by the following procedure. The calcium soap dispersion was prepared by adding 10 mL hard water prepared on the basis of the reported method[8] and 15 mL deionized water into 5 mL of 5 g/L of the sodium oleate solution in 50 mL colourimetric tubes. To the above calcium soap dispersion was added different loadings of the detergent builders. After the dispersion was mixed at 60 ºC for 5 min, the transmittance of the dispersion at 450 nm of wavelength was detected by a UV755B UV spectrophotometer (Shanghai Precision Scientific Instruments Co., Ltd). On the same loading of the builders, higher transmittance of the dispersion shows better dispersing ability for calcium soap.

The buffering pH capacity was evaluated by the following procedure. At room temperature, 100 mL 1 wt % of the builder solutions was titrated with 3 mol/L of hydrochloric acid solution and the volume consumption of hydrochloric acid solution was recorded when pH dropped to a certain value. The more the consumption of the hydrochloric acid solution, the better the buffering pH capacity. The 1 wt % of the polymer solutions were made by directly diluting the mother liquid of the polymerization. The pH was measured using pHS-25 digital pH meter (Shanghai zhiguang Instrument Co. Ltd.). The surface tension of solutions was measured at ambient temperature by a JZHY-180 Interfacial Tensiometer (Germany Brook's spectrum apparatus Company).

The cloths stained with oil and carbon black for detergency test were prepared according to Chinese standard GB/T 13174-2003. The standard laundry powder was prepared by grinding and mixing all the ingredients listed in Table-1. The powder (I), powder (II) and powder (III) were prepared in the same manner except to replace sodium tripolyphosphate by the dried powders of AA-Co-IA, AA-Co-MA and AA-Co-IA-Co-MA respectively.

TABLE-1
FORMULATION OF THE STANDARD LAUNDRY POWDER

Ingredient	Weight (%)
Sodium dodecyl benzenesulfonate	15
Sodium tripolyphosphate	17
Sodium silicate	10
Sodium carbonate	3
Carboxylmethylcellulose	1
Sodium sulfate	54

The detergency tests were carried out according to Chinese standard GB/T 13174-2003. The detergency was calculated by the following equation:

$$R = \Sigma (F2-F1)/3$$

where, R is the detergency, %; F1 and F2 are the whiteness value of the test cloths before washing and after washing respectively. Whiteness values were determined repeatedly three times.

In order to determine anti-sediment ability of the powder, the white cloths were also washed at the same time in the determination of detergency. The anti-sediment ability was calculated using the following equation:

$$T = \Sigma (F2-F1)/3$$

where, T is the anti- sediment ability of the powder, %; F1 and F2 are the whiteness value of the white cloths before washing and after washing. The smaller T value indicates the lower contamination, *i.e.*, the better anti-sediment ability of the powder.

The whiteness was measured using a WS-SD d/o whiteness meter (Wenzhou Instrument Co., Ltd).

Evaluation of biodegradability: To 200 mL 5 % of the copolymer solutions in 500 mL beakers was added a small amount of aerobic bacteria. When the bacteria were cultivated in airing for 0 d,7 d and 28 d, the CODCr values of solutions were measured respectively by potassium dichromate method according to Chinese standard GB11914-89. The bacteria were filtered out before measurement. The biodegradation rate of the copolymers was calculated using the following equation:

$$Bd = (\text{CODCr } 0 - \text{CODCr } n)/\text{CODCr } 0 \times 100\ \%$$

where, Bd is the biodegradation rate of the polymer, %; CODCr 0 and CODCr n are the CODCr value of the polymer solution when the cultivation time is 0 d and n d respectively.

RESULTS AND DISCUSSION

Dispersibility for calcium soap: As shown in Fig. 1, the transmittance of the calcium soap dispersion containing AA-Co-IA is obviously higher than that containing AA-Co-MA, AA-Co-IA-Co-MA and sodium tripolyphosphate in the same concentration of builders, which indicates that the dispersibility of AA-Co-IA for calcium soap is significantly better than that of AA-Co-MA, AA-Co-IA-Co-MA and sodium tripolyphosphate and the dispersability of AA-Co-IA-Co-MA is slightly better than that of AA-Co-MA and sodium tripolyphosphate, but the dispersibility of AA-Co-MA was slightly poorer than that of sodium tripolyphosphate. Sodium polycarboxylates can be adsorbed on the calcium soap particles, which can form a hydrophilic hydrate layer that exhibits a steric effect to prevent the particle coagulation. In addition, the ionized carboxyl groups on the surface of the particles also provide electrostatic repulsion to further prevent the coagulation. For this reason, sodium polycarboxylates have good dispersibility for calcium soap, which is related to the content of carboxyl in the molecular chain. By comparison of the monomer conversions and the above results, it is found that the dispersibility of the copolymers is relevant to the monomer conversion. The polymerization activity and copolymerization ability of itaconic acid are higher, so the monomer conversion of the AA-Co-IA is higher, which brings about higher carboxyl content in the molecular chain of the AA-Co-IA and better dispersibility.

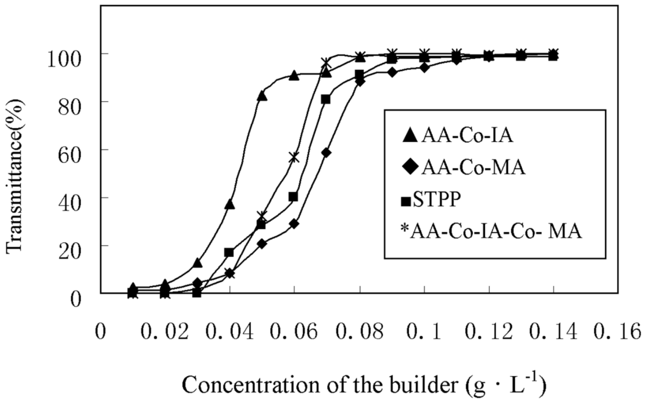

Fig. 1. Relation between the transmittances of calcium soap dispersions and the concentrations of the builders

Buffering pH capacity: As can be seen in Fig. 2, when the pH of the solutions is adjusted to the same value, the consumption of the hydrochloric acid solution by the AA-Co-IA solution is slightly more than that by the AA-Co-MA solution and the AA-Co-IA-Co-MA solution and the consumption by the AA-Co-MA solution is almost the same as that by the AA-Co-IA-Co-MA solution and all the consumptions by the three copolymer solutions are more than that by sodium tripolyphosphate. This shows that the buffering pH capacity of the AA-Co-IA is slightly larger than that of the AA-Co-MA and the AA-Co-IA-Co-MA and the buffering pH capacity of the AA-Co-MA is almost the same as that of the AA-Co-IA-Co-MA and all the buffering pH capacities of the three copolymers are larger than that of sodium tripolyphosphate. Because the coexistence of -COOH and -COONa in the molecular chain of the sodium polycarboxylates in the vicinity of pH = 7 forms the buffer system, they possess stronger buffering pH capacity, which is related to the carboxyl contents in its molecular chain. The higher the carboxyl content, the stronger the buffering pH capacity. Just as mentioned above, the carboxyl content in the molecular chain of AA-Co-IA is higher than that of the AA-Co-MA and AA-Co-IA-Co-MA, so the buffering pH capacity of the former is stronger than that of the latter.

Surface activity: The relation between the surface tensions of various builder solutions and their concentrations is presented in Fig. 3. When the concentration of builders is 1 wt %, the surface tension of the AA-Co-MA solution is only 54 mN/m, that of the AA-Co-IA-Co-MA solution is 59 mN/m, but that of the AA-Co-IA solution and sodium tripolyphosphate solution are about 65 mN/m, which reveals that the surface activity of the AA-Co-MA is stronger than that of the AA-Co-

IA-Co- MA, the AA-Co-IA and sodium tripolyphosphate. The structure consisting of the lipophilic c-c main chains and the hydrophilic -COO⁻ side chains results in the surface activity of sodium polycarboxylates. The higher carboxyl content in the molecular chain of AA-Co-IA makes it more hydrophilic, so its surface activity is lower. From Fig. 3, it can be clearly seen that the detailed relation of each builder solution is complex, so the further study will focus on this phenomenon.

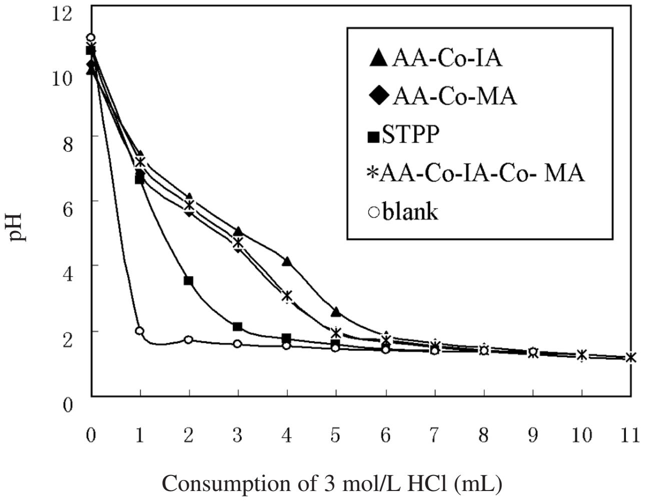

Fig. 2. Relation between the pH value of builder solutions and the volume consumption of 3 mol/L HCl

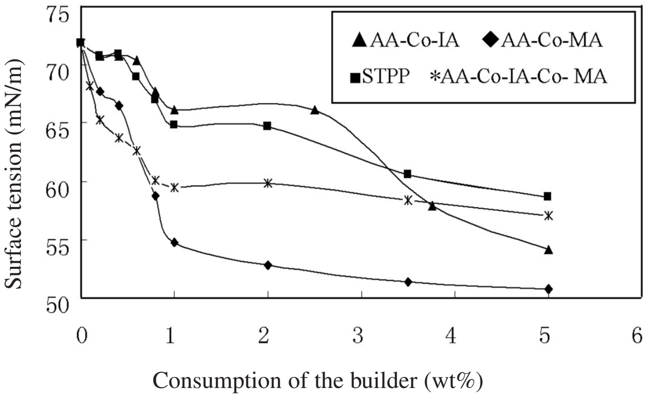

Fig. 3. Relation between the surface tensions of the builder solutions and their concentrations

In the presence of 2 wt % of the builders, the relation between the surface tension of LAS solutions and its concentration is shown in Fig. 4. The result reveals that the presence of the AA-Co-IA, the AA-Co-MA, the AA-Co-IA-Co-MA and sodium tripolyphosphate has significant effect on the surface activity of the LAS solution. The surface tensions of 1 mol/L LAS solution decrease from about 46 mN/m (without the builders) to 30 mN/m by incorporating 2 wt % of the builders, which shows that all the above four builders have good synergistic effects with LAS. The above four builders are all electrolytes. Their Na^+ can be adsorbed on the surface adsorption layer of LAS, which reduces the repulsion of the anion of LAS in the surface adsorption layer and tighten the layer, so increases the surface activity of the LAS.

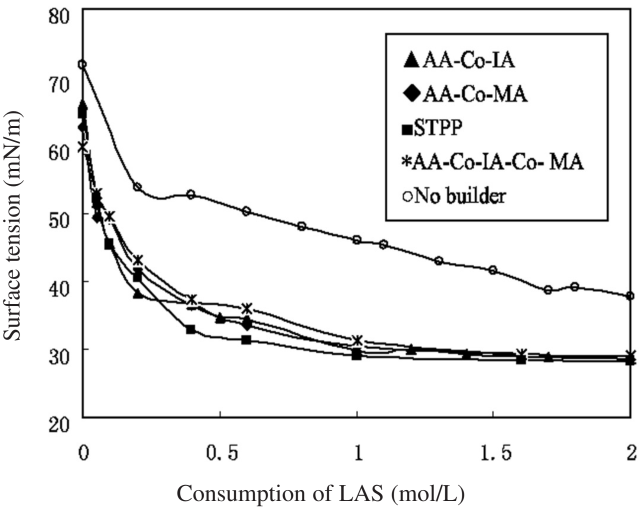

Fig. 4. Relation between the surface tension of LAS solutions and its concentration in the presence of 2 wt % of the builders

Detergency and anti-sediment ability: From the results of Table-2, the detergency and anti-sediment ability of laundry powder I prepared using the AA-Co-IA replacing sodium tripolyphosphate are better than the standard laundry powder. The detergency of laundry powder II prepared using the AA-Co-MA replacing the sodium tripolyphosphate is slightly poorer than the standard powder, but the anti-sediment ability of the former is slightly better than the latter. The detergency of laundry powder III prepared using the AA-Co-IA-Co-MA replacing the sodium tripolyphosphate is obviously better than that of the standard powder, but its anti-sediment ability is markedly poorer than that of the standard powder. In a word, The balance detergent performance of the AA-Co-IA is better than that of the AA-Co-MA, the AA-Co-IA-Co-MA and sodium tripolyphosphate. But economically the powders made using the copolymers replacing sodium tripolyphosphate quantitatively will be more expensive than the standard one. In order to reduce the total cost of laundry powders containing the AA-Co-IA, it is suggested that the AA-Co-IA is used in combination with some cheap detergent builders such as 4A zeolite and δ-layered sodium disilicate.

TABLE-2
DETERGENT PROPERTY COMPARISON BETWEEN THE COPOLYMERS AND STPP

Laundry powder	Builder	R (%)	T (%)
Standard powder	STPP	36.40	1.45
Powder I	AA-Co-IA	39.53	0.61
Powder II	AA-Co-MA	35.8	1.25
Powder III	AA-Co-IA-Co-MA	38.99	1.68

Biodegradability: In Table-3, the biodegradation rates of the AA-Co-MA, the AA-Co-IA-Co-MA and the AA-Co-IA in 7 day are 14.2, 13.0 and 19.4 % respectively and the rates in 28 day are 18.3, 16.0 and 42.5 % respectively, which shows that the AA-Co-IA can be biodegraded with ease, but the AA-Co-MA and the AA-Co-IA-Co-MA are difficult to biodegrade. It is wonderful and difficult to understand that the biodegradability of the AA-Co-IA-Co-MA is poorer slightly than that of the AA-Co-MA.

TABLE-3
RESULTS OF BIODEGRADABILITY OF THE COPOLYMERS

Copolymer	Biodegradability (%)	
	7 d	28 d
AA-Co-MA	14.2	18.3
AA-Co-IA-Co-MA	13.0	16.0
AA-Co-IA	19.4	42.5

Conclusion

All itaconic acid and maleic anhydride contains two carboxyl groups, but the polymerization activity and the copolymerization ability of itaconic acid with acrylic acid are higher than that of maleic anhydride due to the different molecular structure. The monomer conversion of AA-Co-IA is higher than that of AA-Co-MA and the carboxyl content in the molecular chain of AA-Co-IA is higher than that of AA-Co-MA, which results in better balance detergent performance of the AA-Co-IA, such as detergency, anti-sediment ability, dispersibility for calcium soap and buffering pH capacity, but the surface activity of the AA-Co-IA is lower. All the three copolymers have a good synergism with sodium dodecyl benzenesulfonate (LAS), so the surface tension of the LAS solution is lowered obviously by incorporating them. It is more important that itaconic acid is made from renewable biomass resources, so the AA-Co-IA can be biodegraded with ease. But economically the powders made using the AA-Co-IA replacing sodium tripolyphosphate quantitatively will be more expensive than that of the standard one. In order to reduce the total cost of laundry powders containing the AA-Co-IA, the AA-Co-IA can be used in combination with some cheap detergent builders such as 4A zeolite and δ-layered sodium disilicate.

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