

Ionomers made from copolymers with uniform grafts

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Summary

Carboxylic acid-containing graft copolymers with uniform polystyrene grafts were synthesized by copolymerization of methacrylate-terminated polystyrene macromers, acrylic acid and butyl acrylate. The graft copolymers were neutralized with metal ions in solution or in melt to form ionomers, which were characterized by IR, TEM and dynamic mechanical analysis. TEM photographs showed that there appeared three phases in the ionomers, namely polystyrene domains, ion clusters and continuous phase of polybutyl acrylate, while dynamic mechanical analysis indicated the phase separation of polystyrene and ion-containing polyacrylate.

Introduction

Graft copolymers made from macromers contain characterized grafts with uniform and predetermined molecular weight. If the macromer exhibits high glass transition temperature, the grafts in the copolymer obtained will form domains, which act as physical cross-linkage between macromolecules. Ionomers are the copolymers containing less than 10 mol % combined ions and also show crosslinking effect due to the ion aggregates existing in the ionomers. Milkovich and his coworkers(1,2) first reported the preparation of graft copolymers from polystyrene macromer and acrylic esters. MacKnight(3) and Eisenberg(4) reviewed the synthesis and structure of several ionomers. Recently McGrath et al(5) reported the synthesis of the ionomers made from block copolymers of polystyrene and polymethacrylic acid.

This paper deals with the synthesis and characterization of ionomers made from copolymers of butyl acrylate and acrylic acid with uniform polystyrene grafts in order to study the new polymer with multiphase structure composed of ion aggregates and polystyrene domains.

Experimental

Materials

Styrene, butyl acrylate and acrylic acid were purified by removal of inhibitors and then distillation under reduced pressure as usual. The purified monomers were stored in a refrigerator before use. AIBN was recrystallized from ethyl alcohol. Benzene was dried by standing over 4A molecular sieve overnight.

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Tetrahydrofuran was dried by distillation over CaH_2 . Ethylene oxide was successively distilled over KOH and CaH_2 . Methacryloyl chloride was synthesized from methacrylic acid and sulfonyl chloride and purified by distillation. Solution of n-butyl lithium in cyclohexane was self-made and its concentration was determined by Gilman double titration(6).

Preparation of polystyrene macromers

To a 20% solution of styrene in benzene was dropped via microsyringe n-butyl lithium solution containing tetrahydrofuran at a molar ratio of 2:1 to n-butyl lithium, until the solution changed to slight yellow in order to remove the impurities in the system. Then a calculated amount of n-butyl lithium was added and the polymerization carried out at 50°C for 2 h. Ethylene oxide was bubbled in until the red color of living polystyrene anions disappeared. The reaction was continued at 50°C for half an hour. Then methacryloyl chloride(MAC) at a molar ratio of $\text{MAC:n-BuLi}=1.5:1$ was introduced via syringe and reacted with the living anions at 45°C for 2 h. The product was precipitated from ethyl alcohol and vacuum dried.

Synthesis and purification of the graft copolymers

To a solution of the polystyrene macromer in benzene was added butyl acrylate and acrylic acid. The ratio of total monomers to benzene is equal to 1g:1.5ml. Solution of AIBN in benzene(0.15% based on the weight of monomers)was charged to the monomer solution under nitrogen atmosphere. Polymerization was carried out at $62\pm 1^\circ\text{C}$ for 24 h. After removal of solvent the product was vacuum dried. Grafting efficiency or the conversion of macromer was determined by the peak area of copolymer divided by the total peak area of both the copolymer and macromer in GPC(LC-4A). The crude copolymer was extracted with n-butyl alcohol and a mixture of petroleum ether and decalin successively. The residue was washed with petroleum ether and ethyl alcohol and vacuum-dried.

The number average molecular weight of the purified copolymer was determined by Bruss osmometry and the carboxylic acid % measured by titration with alcoholic solution of sodium hydroxide using phenolphthalein as indicator and acetone as solvent.

Preparation of ionomers

The graft copolymers containing acid groups can be neutralized in solution by dissolving the graft copolymer in acetone followed by neutralization with 0.1N solution of sodium hydroxide in ethyl alcohol at room temperature for 2 h or with 1% solution of zinc acetate in methyl alcohol at 50°C for 24 h. The product was precipitated, washed with water and then vacuum dried. Zinc content of the ionomer obtained may be determined by first igniting the sample in muffle furnace at 480°C for 10 h and then treating with hydrochloric acid. The zinc ions dissolved were titrated with EDTA.

The graft copolymer containing carboxylic acid group can also be neutralized in melt by plasticizing it at $160\text{-}165^\circ\text{C}$ and 30 rpm in Brabender Plasticorder followed by adding equivalent amount of solid metal acetate. The mixing torque values were recorded at 5 min intervals, until the torque value no longer changed. The ionomer obtained was vacuum dried.

Characterization of the ionomers

The ionomers were characterized by IR, transmission electron microscopy and dynamic mechanical analysis. IR spectra of both the ionomer and its original graft copolymer were recorded with a PE-580B infrared spectrophotometer using pressed thin film. Microphotographs of lead ionomers made from the graft copolymer and also from a copolymer of butyl acrylate and acrylic acid were taken by a TEM-100C transmission electron microscope. The samples were prepared by swelling the lead ionomers in toluene, then adding n-butyl alcohol to dissolve it and form film on copper sieve. Dynamic mechanical properties of the ionomer were measured with a RHEO-200 viscoelastometer with 3.5 Hz frequency and a heating rate of 3°C/min, using a sample of 0.2-0.5mm thickness.

Results and discussion

The terpolymerization of polystyrene macromer with butyl acrylate and acrylic acid.

Copolymerization of polystyrene macromer with butyl acrylate has been studied in our previous paper(7). Here will be discussed the effect of acrylic acid on the terpolymerization. Fig. 1 shows that the grafting efficiency increases with increase of acrylic acid used. Acrylic acid seemed more easily to copolymerize with the macromer than butyl acrylate probably due to the less steric hindrance of acrylic acid. Time for the appearance of elution peak for the copolymer in the GPC decreases with increase of acrylic acid, or roughly saying, molecular weight of the copolymer increases with increasing acrylic acid.

Through analysis of the products taken at different intervals of polymerization, the relationship between the polymerization time and individual conversions of the two monomers and one macromer was shown in Fig. 2. It can be seen that at the beginning of polymerization the macromer copolymerized more quickly than the two monomers. This can be interpreted that the reactivity of the double bonds in the methacryloyl group is larger than that in the acryloyl group. However, as polymerization proceeded, viscosity of the polymerization system increased, which

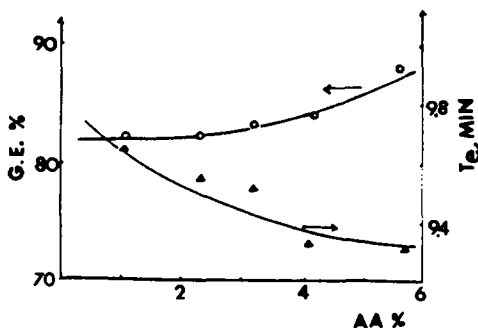


Fig. 1. Effect of acrylic acid on the grafting efficiency(G. E.) and elution time (T_e) of the grafting copolymer

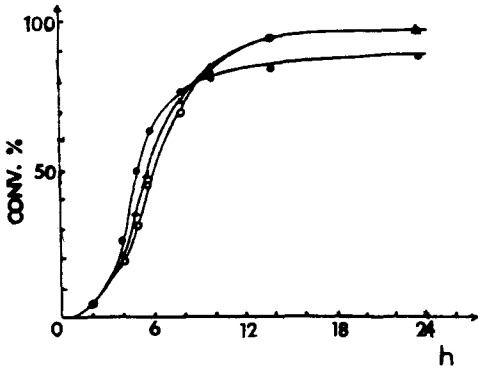


Fig. 2. The relationship between polymerization time and individual conversions of :●—macromer;▲—butyl acrylate;◻—acrylic acid.

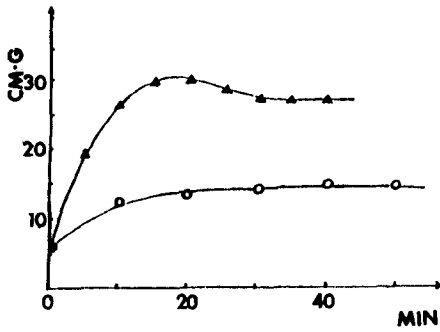


Fig. 3. Plastograph torque(g·cm) as a function of neutralization time, using neutralizing agent:▲—magnesium acetate;◻—zinc acetate.

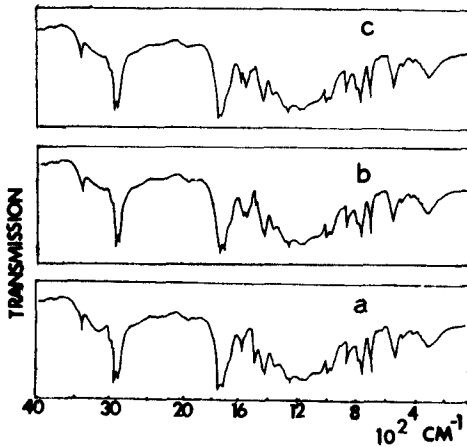


Fig. 4. IR spectra of the a) graft copolymer, b) sodium ionomer, c) zinc ionomer

caused the diffusion of the macromer more difficult. Thus the probability for the reaction of macromer became less and less, so that at the end of polymerization the individual conversion of the macromer was lower than that of the two monomers. The individual conversion of butyl acrylate seems somewhat faster than that of acrylic acid at the beginning probably due to the higher concentration of butyl acrylate used.

The crude copolymer obtained can be purified by extraction with butyl alcohol to remove homopolymer and copolymer of acrylate, followed by extraction with a mixture of decalin and petroleum ether to remove homopolystyrene. The purified graft copolymer looks more transparent than the crude one.

The structural parameters of some purified graft copolymers were shown in Table 1. When the polystyrene content is higher than 18% and the number average molecular weight of the macromer is $6-14 \times 10^3$, the average number of grafts per molecule is 3-7 and the number average molecular weight of segments between grafts is $2.5-7.1 \times 10^4$, while that between acid groups is $1-2 \times 10^4$, when acrylic acid content is 2-6%.

Preparation of ionomers from the graft copolymers

When neutralization of graft copolymers containing carboxylic acid groups with zinc acetate was carried out in acetone-methanol at 50°C , zinc ions combined in the product increased rapidly at the beginning within 10 h, then slowly till to equilibrium within 24 h. When neutralization was performed in Brabender plasticorder at $160-165^\circ\text{C}$ and 30 rpm, the reaction proceeded more quickly than that in solution. If zinc acetate was used in neutralization, the mixing torque increased to a constant value within 40 min, as shown in Fig. 3. If magnesium acetate was used instead of zinc acetate, the mixing torque increased to a higher constant value within 30 min. This indicates that magnesium ionomer exhibits a higher melt viscosity and zinc ionomer showed better processing properties.

Characterization of the ionomers

IR spectra of the purified graft copolymer and its sodium or zinc ionomer were shown in Fig. 4 a), b), c) respectively. A characteristic peak at 1730 cm^{-1} is due to the carbonyl group, while that at 3250 cm^{-1} is from the hydroxyl group. Peaks at $2960-2990\text{ cm}^{-1}$ are for the CH_2 and CH_3 groups. Absorption at $940-960\text{ cm}^{-1}$ is due to the butyl ester group and that at 1600 and 3040 cm^{-1} is for the benzene ring. Characteristic absorption of metal carboxylate appears at 1560 cm^{-1} . It can be seen that the characteristic peaks for the carboxylic acid group almost disappear and the Table 1. Structure Parameters of Some Samples of the Acid-containing Copolymers with Uniform Grafts

$M_{nc} \times 10^{-4}$	$M_{ng} \times 10^{-4}$	W% _g	W% _A	N_g	$M_{nb} \times 10^{-4}$	$M_{nA} \times 10^{-4}$
18	1.1	18.4	1.11	3.01	4.88	0.551
22	1.1	18.8	5.62	3.76	4.75	0.103
15	1.1	8.66	3.58	1.18	11.6	0.187
24	1.1	30.2	2.46	6.59	2.54	0.219
19	0.67	20.4	3.10	5.79	2.61	0.188
25	1.4	18.2	3.10	3.25	7.06	0.193

* M_{nc} — M_n of the copolymer; M_{ng} — M_n of the polystyrene grafts; W%_g—wt% of styrene; W%_A—wt% of acrylic acid; N_g —no. of grafts; M_{nb} — M_n of segments between the grafts; M_{nA} — M_n of segments between the acid groups

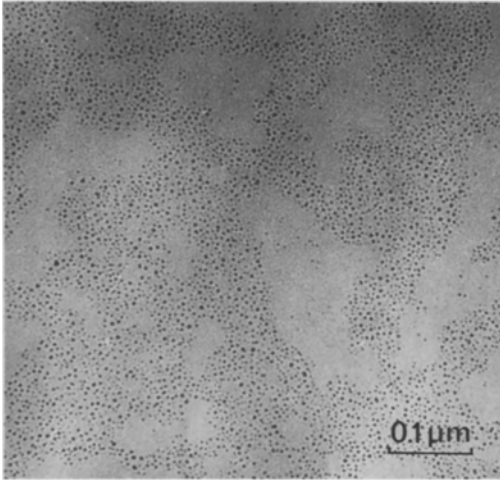


Fig. 5. TEM photograph of the lead ionomer made from the graft copolymer with 2.33 wt% of acrylic acid

absorption peak for the metal carboxylate appears after neutralization of the graft copolymer. This demonstrates that sodium or zinc ions react significantly with the carboxylic acid groups of the graft copolymer during neutralization.

Microphotographs of the lead ionomers obtained from the graft copolymer was shown in Fig. 5. There appear three phases: the large bright region represents the polystyrene domain, the black spots denote the lead ion clusters, and the region containing the black spots is the continuous phase of polyacrylate. When the lead ionomers were synthesized without polystyrene macromers, then no bright domain was observed under transmission electron microscope (Fig. 6).

Dynamic mechanical analysis indicated that two glass transition temperatures occurred at about -12 and 95°C . This implies that there exists microphase separation in the ionomers. The higher transition temperature represents the glass transition temperature of polystyrene domains, while the lower transition temperature denotes the glass transition temperature of the continuous phase of polyacrylate containing ion multiplets (Fig. 7).

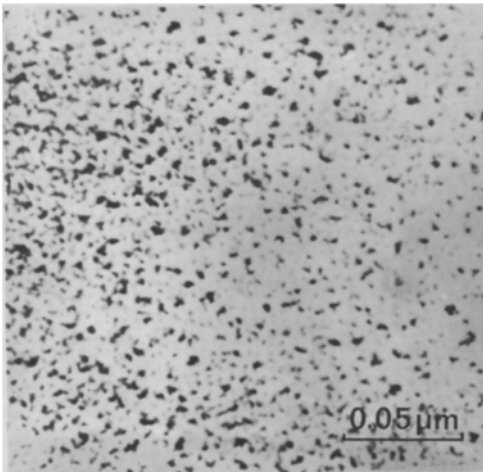


Fig. 6. TEM photograph of the lead ionomer made from copolymer of butyl acrylate and acrylic acid with 7.12 wt% of acrylic acid

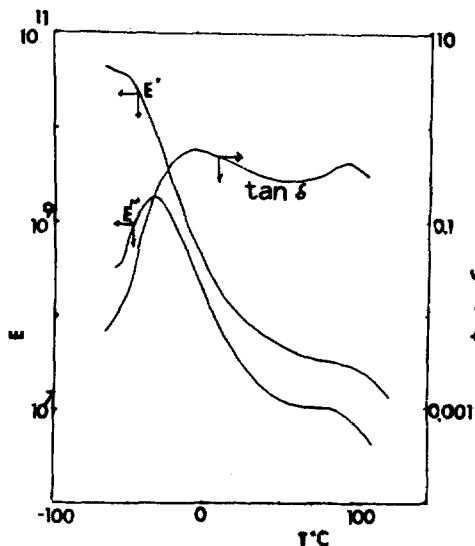


Fig. 7. Dynamic mechanical spectrum of the ionomers made from the graft copolymer.

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