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ORIGINAL CONTRIBUTION

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Synthesis of multiblock ionomers by copolymerization in inverse microemulsions

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Abstract The synthesis of ionomers with randomly distributed ionic blocks was achieved by free radical copolymerization of a hydrophobic monomer with an ionic comonomer in inverse microemulsions. The ionic monomer, sodium acrylate (approximately 1 mol% based on the monomer feed) is encapsulated in the aqueous compartments of inverse micelles of sodium bis-(2-ethylhexyl)sulfosuccinate. The hydrophobic monomer, methyl methacrylate or butyl acrylate, is dissolved together with the initiator in the oil continuous phase (toluene). For a given hydrophobe/ionic monomer ratio, it is possible to tune the length of the ionic block in the ionomer by adjusting the initial number of ionic monomers per water droplet, N_H. The ionomers were obtained in their Na salt form and converted thereafter into Ca salts. Differential scanning calorimetry measurements performed on both series show a decrease in the glass-transition temperature for the Ca-poly(methyl methacrylate) ionomers upon increasing N_H. The results are discussed in terms of the nature of the counterion and of the ionomer microstructure.

Key words Multiblock poly(methyl methacrylate) and poly(butyl acrylate) based ionomers · Inverse microemulsion · Sodium polyacrylate · Sodium bis(2-ethylhexyl)sulfosuccinate · Differential scanning calorimetry

Introduction

In the past decade, the synthesis of hydrophobically modified polyacrylamides by means of a micellar polymerization process was thoroughly investigated by several groups [1]. The incorporation of a few hydrophobic groups in the hydrophilic macromolecular chain results in systems with unique rheological characteristics. In aqueous solution, above a certain concentration, the hydrophobic groups associate intermolecularly and build up a transitory network. In this process, the hydrophobic monomer is solubilized within surfactant micelles, whereas the hydrophilic monomer is dissolved with the initiator in the aqueous continuous medium (Fig. 1a). This method of synthesis leads to water-soluble polymers containing randomly distributed hydrophobic blocks along the hydrophilic backbone. By adjusting the surfactant-to-hydrophobe molar ratio, one can tune the length and the number of the blocks. It has been shown that the associating behavior of these copolymers is strongly dependent on their microstructure (i.e. upon the length and number of blocks for a given hydrophobe content) [2, 3].

These novel results prompted us to reverse the aqueous micellar copolymerization process into its “mirror” image, with the aim of synthesizing ionomers, which are hydrophobic copolymers containing a small molar percentage of an ionic component. The incorporation of ionic units strengthens the mechanical properties of the basic polymer, owing to the formation of ionic multiplets embedded in the backbone matrix and acting as cross-links between different chains through electro-

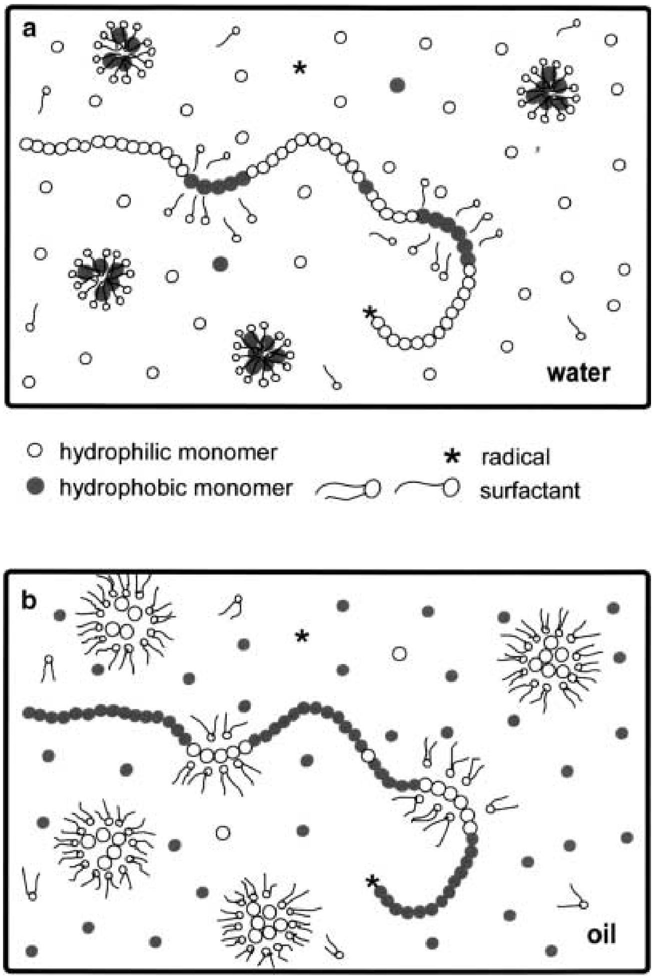

Fig. 1 Schematic representation of the micellar copolymerization process in **a** aqueous and **b** organic media

static interactions [4, 5]. A parallel can be drawn between ionomers and hydrophobically modified water-soluble polymers. Both exhibit associating properties: for ionomers they are mediated by electrostatic interactions and for hydrophobically modified water-soluble polymers they are mediated by hydrophobic interactions.

Among the various types of ionomer structures that can be achieved synthetically, random copolymers, block copolymers and telechelics have been the most thoroughly investigated [5]. To our knowledge, the synthesis of multiblock ionomers has not yet been reported and the question addressed in this article is whether the distribution of the ionic species along the polymer chain can be controlled within the scheme of micellar copolymerization.

For the synthesis of ionomers, the corresponding "mirror" image of the aqueous micellar medium consists of water-swollen micelles containing a few molecules of the ionic component, dispersed in an organic continuous phase in which the hydrophobic (main) monomer is solubilized. The polymerization is initiated in the organic phase with oil-soluble radicals (Fig. 1b).

An additional advantage of this technique rests in the direct access to ionomers in a one-step reaction as compared to classical copolymerizations in homogeneous media which require a subsequent neutralization. Vaskova et al. [6, 7] synthesized copolymers of methyl methacrylate (MMA)/acrylamide and styrene/acrylamide in an inverse microemulsion medium, where the two monomers were dispersed in the different phases, but the scope of these studies was not the synthesis of ionomers. The copolymers obtained were water-soluble as they contained mainly acrylamide. Nuno et al. [8] prepared ionomers based on styrene and sodium acrylate (NaA) by one-step emulsion polymerization, but the materials obtained were rather heterogeneous in composition.

In the present article, we describe the synthesis of multiblock ionomers based on MMA/NaA and butyl acrylate (BA)/NaA in an inverse microemulsion medium, where the water pools are formed by the surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) dispersed in toluene. For comparison, the corresponding homopolymers of MMA and BA were also synthesized in the same reaction medium as the ionomers. The polymerization kinetics was followed and the ionomers characterized. The influence of the microstructure of the ionomers on their macroscopic properties in the solid state was studied by differential scanning calorimetry (DSC).

Materials and techniques

Materials

AOT was purchased from Fluka and was purified as described elsewhere [9]. It was further dried in a dessiccator over P_2O_5. NaA was obtained from Aldrich and was used as received. MMA and BuA were distilled under reduced pressure over N_2 and were used immediately afterwards. MMA was passed through a column (Aldrich) to remove the stabilizer. Toluene (Carlo Erba p.a.) was refluxed over sodium and distilled before use. Water was purified by reverse osmosis (Milli-Ro 3 + , Millipore) and followed by ion exchange and filtration steps (Milli-Q, Millipore). The hydrophobic initiator, azobis(isobutyronitrile) (AIBN), was recrystallized in ethanol, dried under vacuum and stored at low temperature. Dibenzoyl peroxide (BPO) was dissolved in chloroform, precipitated with methanol and dried in a vacuum. The initiators were dissolved in a few milliliters of toluene and were added after the formation of the microemulsions.

The microemulsions were prepared by adding water or a water/NaA mixture to a solution of AOT in toluene/MMA (toluene/BA) mixture in the desired proportions. A typical batch consists of 85 g (77.8 wt%) toluene, 15 g (13.7 wt%) AOT, 6 g (5.5 wt%) MMA, 0.0564 g NaA, 3.11 g (2.9 wt%) H_2O and 0.072 g AIBN.

Polymerization procedure

Nitrogen was bubbled through the transparent microemulsion for about 45 min at room temperature to eliminate oxygen. Then the mixture was transferred into the reactor and heated to the reaction temperature (60 °C), followed by addition of the initiator. The systems remained stable and transparent during the duration of the polymerization (between 400 and 1200 min). The reaction was stopped by pouring the solution into a sixfold excess of methanol and kept overnight in a refrigerator. The supernatant liquid was decanted and the polymer was washed with methanol and centrifuged (15 min at 9000 rpm) repeatedly. Both polymers were dissolved in benzene; the BA samples were evaporated and kept under vacuum for 2 days at 40–50 °C; the PMMA samples were freeze-dried. For the kinetics studies, small aliquots (5 ml) of the reaction mixture were taken out at different time intervals and precipitated in a tenfold excess of methanol, washed and dried as described earlier.

Determination of copolymer composition

The polymer in its salt form was converted to its acidic form using an ion-exchange resin. Polymer (100 g, weighed accurately) was dissolved in a water/tetrahydrofuran (THF) mixture (90/10, v/v). A strong acid ion-exchanger resin (Merck type I) was conditioned with the same solvent and the polymer solution was passed through the column which was rinsed with the solvent of 5 times the column volume. (250 ml). The eluate was evaporated to 50 ml total volume under reduced pressure at 30–40 °C. The final solution was titrated potentiometrically (Metrohm 605 pH electrode) with a solution of 0.01 N NaOH in THF/H_2O 50/50, v/v.

Formation of Ca divalent salts

The Ca-PMMA ionomers were prepared from the corresponding Na ionomers according to the method of Ma et al. [10]. Polymer (200 mg) was dissolved in 10 ml benzene/methanol (90/10, v/v) and 4 ml 1 N HCl was added. The mixture was heated to 85–90 °C while stirring on an oil bath to evaporate the organic solvents. At about 80 °C, the copolymer in its acidic form precipitates as a white foam, which was washed, dried and milled into a powder and washed again with deionized water five times to remove the remaining HCl. The dried powder was redissolved in benzene/methanol (90/10, v/v) and neutralized with an excess of $Ca(OH)_2/H_2O$ solution (0.04 N). The two-phase reaction mixture was stirred vigorously overnight. The Ca ionomer was precipitated from methanol, redissolved in benzene/methanol (90/10, v/v) and freeze-dried.

The same procedure could not be applied to BA-based ionomers owing to experimental difficulties arising from the low value of the glass-transition temperature of BA ($T_g = -54$ °C).

DSC analysis

The DSC curves of the ionomer samples (10 mg) were recorded using a Perkin Elmer DSC 7 apparatus. The heating and cooling rates were set at 10 °C min^{-1}. For each sample, three heating and cooling cycles were made to exclude the influence of the thermal sample history. Usually, the T_g values of the second and third heating cycles were the same and the latter thermograms were used for analysis. The T_g were determined by the intersection method.

Results and discussion

Ionomer synthesis

H_2O/AOT/oil ternary systems have been the object of numerous studies and their structural properties have been investigated using various techniques [11, 12]. In most cases, aliphatic hydrocarbons such as heptane or isooctane were used. Nevertheless, in our study, this kind of oil is not suitable, owing to the insolubility of the growing polymer chains during the reaction. Toluene is an oil of choice in our case since it is a good solvent for MMA and BA and for the corresponding polymers. On the other hand, the microemulsion domain of the toluene/AOT/water system is less extended than for systems containing aliphatic oils [13, 14]. As a consequence the compositional freedom for the ionomer synthesis is limited.

For the copolymerization procedure and for the expected polymer microstructure, the number of comonomer molecules per micelle, N_H, is a crucial parameter. This parameter can be expressed as the molar ratio of the concentration of the ionic monomer to that of the micelles. The concentration of the micelles strongly depends on the aggregation number, N, of AOT, which is controlled by the molar ratio of the concentration of water to that of AOT, denoted as ω. Literature data for the ω dependence of N are reported in Fig. 2 [14–16]. Nearly linear behavior is observed between $\omega = 3$ and 14, which is the range relevant for the formation of toluene/AOT/water stable globular microemulsions [13]. The linear fit (for $\omega > 3$) $N = a\omega + b$, where $a = 14.5$ and $b = -3.6$, is used to determine the micelle concentration. It follows that

$$N_H = [\text{ionic monomer}](14.5\omega - 3.6)/[\text{AOT}] \qquad (1)$$

For a given system, Eq. (1) allows the determination of N_H. This procedure is illustrated in Fig. 3, where the dependence of N_H on the water content (expressed through ω) is plotted for different comonomer contents

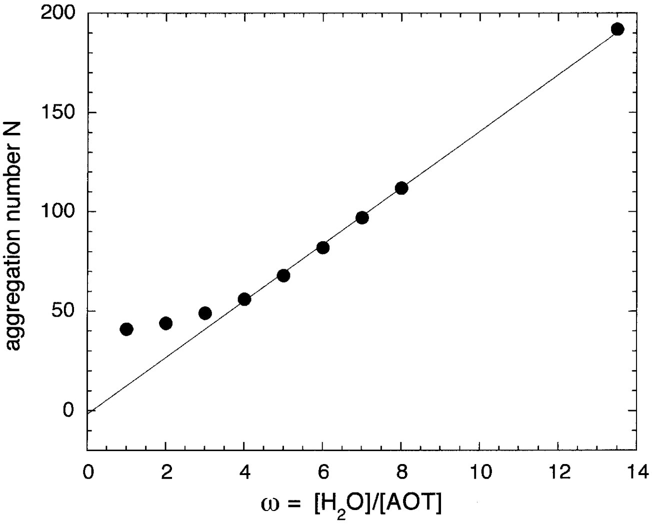

Fig. 2 Aggregation number of sodium bis(2-ethylhexyl) sulfosuccinate (*AOT*) versus the molar ratio $\omega = [H_2O]/[AOT]$ (data from Refs. [14–16])

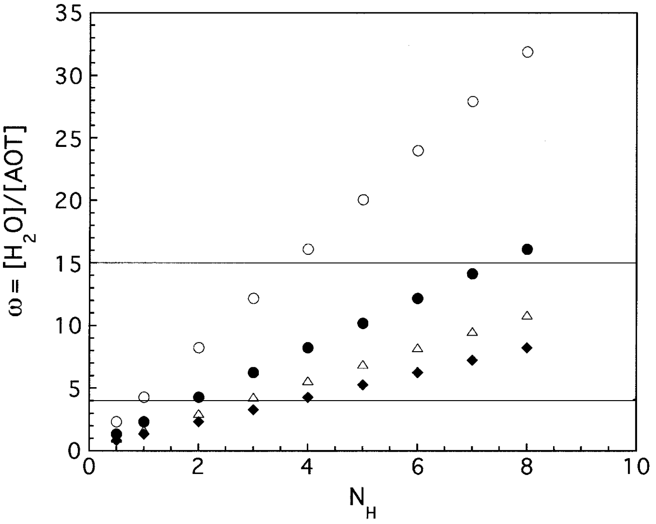

Fig. 3 Variations of ω versus the number of comonomer molecules per micelle (N_H) calculated from the data of Fig. 2 for different sodium acrylate (*NaA*) contents with respect to the monomer feed (mol%): (○) 1; (●) 2; (△) 3; (◆) 4. Batch composition: 100 g toluene, 20 g AOT and 10 g butyl acrylate (*BA*)

in a batch of 20 g AOT, 100 g toluene and 10 g BA. The range of possible combinations of N_H and comonomer content is limited by the phase boundaries of the microemulsion. The values of the reaction parameters used for the synthesis of the ionomers are given in Tables 1 and 2.

Kinetics studies

The conversion–time curves for the homopolymerization and the copolymerization of MMA in an inverse microemulsion medium are reported in Fig. 4a. The upper curve refers to samples initiated with AIBN. The conversion increases steadily with time and levels off to a plateau at about 30% conversion (Table 1). The kinetics of the copolymerization reaction does not differ from that of MMA homopolymerization (filled triangles in the plot) nor does it depend on the microstructure of the ionomers (expressed by N_H and by the number of blocks per chain), owing to the low amount of the ionic comonomer used in the feed (below 2 mol%).

Table 1 Characteristics of poly(methyl methacrylate-*co*-sodium acrylates)

Sample	Polymer synthesis					Polymer characterization		
	NaA (mol%)[a]	N_H	ω = [H$_2$O]/[AOT]	[Initiator] (mol%)[a]	Yield (wt%)[b]	M_w (SEC-MALLS)	Ion content (mol%)[c]	Blocks/chain
M-5	0.0	0.0	14.3	0.76 AIBN	27 (480)	39000	0.0	0.0
M-6	1.06	4.0	14.3	0.77 AIBN	29 (550)	38000	1.30	1.0
M-15	1.01	1.1	5.0	0.71 AIBN	25 (500)	42000	1.29	3.8
M-16	0.99	1.1	5.1	0.72 AIBN	32 (1240)	45000	1.57	4.7
M-17	1.00	2.0	7.0	0.67 AIBN	30 (480)	53000	1.80	3.6
M-18	1.10	3.3	12.3	0.75 AIBN	26 (490)	41000	1.79	1.8
M-21	1.00	1.1	5.0	0.76 BPO	17 (1440)	–	–	–

[a] Based on monomer feed
[b] The numbers in parentheses refer to the time (min) for the yield considered
[c] Found in copolymers

Table 2 Characteristics of poly(butyl acrylate-c*o*-sodium acrylates)

Sample	Polymer synthesis					Polymer characterization		
	NaA (mol%)[a]	N_H	ω = [H$_2$O]/[AOT]	[Initiator] (mol%)[a]	Yield (wt%)[b]	M_w (SEC-MALLS)	Ion content (mol%)[c]	Blocks/chain
B-12	0.0	0.0	7.4	0.37 BPO	13 (810)	85000	0.0	0.0
B-7	1.03	3.6	13.6	0.77 AIBN	36 (1105)	55100	1.50	1.5
B-9	1.05	2.0	7.1	0.84 AIBN	29 (510)	63800	1.30	2.3
B-14	1.01	1.2	4.05	0.80 AIBN	26 (566)	79000	2.30	10.3
B-11	1.11	2.1	7.1	0.49 BPO	29 (433)	70100	1.00	2.0
B-19	1.30	4.0	8.2	0.37 BPO	15 (495)	92500	1.10	1.6
B-13	2.08	3.4	7.0	0.39 BPO	15 (528)	70500	2.75	3.5
B-20	2.95	6.0	8.2	0.42 BPO	19 (850)	80000	2.90	2.5

[a] Based on monomer feed
[b] The numbers in parentheses refer to the time (min) for the yield considered
[c] Found in copolymers

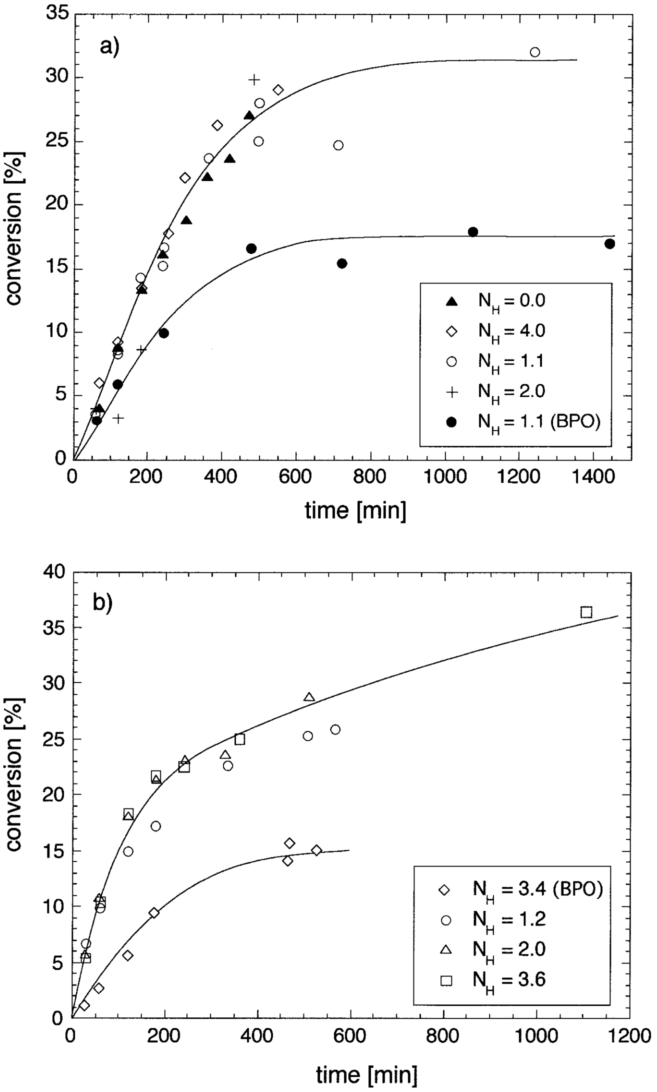

Fig. 4 Conversion–time curves for **a** methyl methacrylate (MMA) and **b** BA copolymerizations initiated with azobis(isobutyronitrile) (*upper curves*) or dibenzoyl peroxide (*lower curves*)

A second oil-soluble initiator, BPO, was tested under the same conditions for the copolymerization of MMA (cf. lower curve of Fig. 4a). It turns out that BPO is less effective than AIBN, in terms of yields (only about 17% conversion was reached) and of reaction times, owing to the lower decay rate, K_d (in toluene: $K_{d(BPO)} = 2.83 \times 10^{-6}$ s^{-1} versus $K_{d(AIBN)} = 9.15 \times 10^{-6}$ s^{-1} [17]). Vaskova et al. [6] reported that, owing to its lower polarity, BPO should be more effective in initiating polymerization in the oil phase than AIBN, which, furthermore, is able to diffuse into the interlayer at the locus of the inverse micelles. Our results tend to show that this effect is not as important as the difference in decay rates. Note that in both cases yields above 30% could not be obtained. Low yield values were also reported by Vaskova et al. [6,7] for the copolymerization of MMA and acrylamide in inverse microemulsions and they were accounted for by dead-end polymerization.

The kinetics of the BA copolymerization initiated with AIBN (about 0.80 mol% with respect to the monomer feed) are shown in Fig. 4b. The behavior is slightly different from that observed in the MMA copolymerization. The initial conversion is higher, about 20% yield being reached after 200 min (compared to 12–15% for MMA samples), then the reaction slows down and finally the conversion levels off at around 35%, as for the MMA polymerization. If a lower amount of BPO is used instead (0.4 mol%), then the kinetics is much slower and smaller yields are obtained, as seen in the lower curve of Fig. 4b.

Characterization of ionomers

Molecular weight

The molecular weights of the homopolymers and the copolymers was determined in THF by size-exclusion chromatography (SEC)–multiangle laser light scattering (MALLS) and by light scattering experiments. When the copolymers were in their ionic form, the measurement was strongly influenced by the formation of aggregates, which caused large errors in light scattering. This effect is also clearly seen in the SEC traces shown in Fig. 5a. The SEC traces of M-6 sample in its Na salt form exhibits at low volume a broad peak, which corresponds to a very high molecular weight. The fact that this peak is only visible in the light scattering detector (solid line) and not in the refractive index increment detector (dotted line) is an indication that only a small fraction is involved in the aggregates. This peak is not seen in the corresponding traces of the copolymer in its acidic form (Fig. 5b) and therefore all the sample characterizations were carried out on the copolymers in their acidic form.

For the PMMA ionomers, typical molecular weights of about 40,000 gmol^{-1} were measured (Table 1), whereas somewhat higher values were obtained for the BA samples (Table 2). All SEC-MALLS traces show a rather narrow molecular-weight distribution, with an index of polydispersity, I_p, ranging from 1.25 to 1.40. These values are low compared to the Schulz–Flory distribution for radical polymerizations, which usually shows values between 1.5 and 2 (for example in the case of PMMA at 60 °C, $I_p \sim 1.8$ as the termination reaction occurs through 40% recombination and 60% disproportionation [18]). Even though the SEC-MALLS technique underestimates somewhat the molecular weight distribution, it could not account for such a low I_p; however, the latter could be related to the loss of some oligomers during the recovery in methanol of the copolymers.

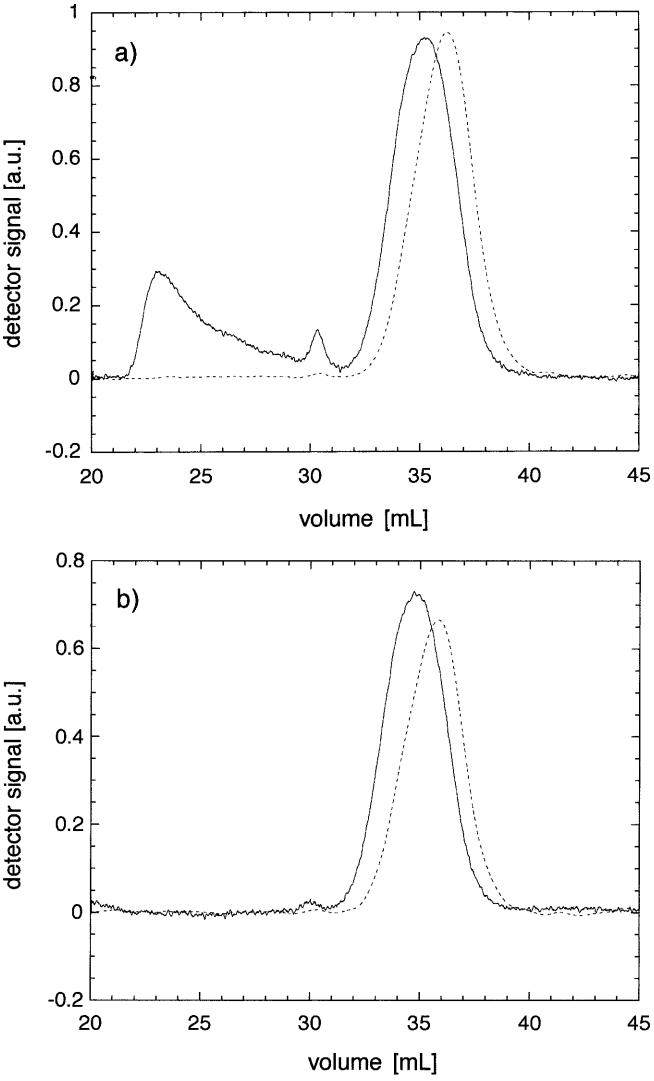

Fig. 5 Size-exclusion chromatography–multiangle laser light scattering of a PMMA-based ionomer (sample M-6) **a** in its Na salt form and **b** in its acidic form. *Solid lines*: light scattering detector; *dotted lines*: refractive index increment detector

Ion content

The content of ionic groups was determined by potentiometric titration of the copolymers in their acidic form. It can be seen from the values reported in Tables 1 and 2 that in most cases the average ionic content in the copolymers is higher than that in the monomer feed, within the experimental error of the measurements (around 10–15%). This result is an indication of some drift in copolymer composition with conversion. A similar effect, although of greater importance, was also observed for polyacrylamides prepared in an aqueous micellar medium and hydrophobically modified with monosubstituted acrylamides [1, 19]. Several causes were invoked to account for the increased reactivity of the comonomer located in the micelles:

1. A microenviroment effect arising from the difference in polarity between the two microseparated phases.
2. Micellar effects (high local concentration, residence time of the propagating radical and exchange dynamics).
3. Different reactivity ratios for the monomer pair involved in the copolymerization.

In this respect and in spite of some scattering in the data, it seems that the drift in copolymer composition for the BA/NaA ionomers, which bear the same polymerizable group, is less than for the MMA/NaA ionomers.

In most of the examples reported in Tables 1 and 2 (1 mol% of comonomer in the feed and about 30% conversion) a full consumption of NaA would result in an ion content of around 3.3 mol%. The values obtained are always smaller (cf. Tables), which suggest that no partial homopolymerization of MMA or BA occurs, despite the compositional drift.

DSC measurements

The incorporation of ionic groups into hydrophobic polymers leads to strengthened mechanical properties. The structure of the ionomers is quite different from that of their corresponding homopolymers. According to Eisenberg et al. [4], the ionic groups aggregate into small structures of tightly packed ion pairs, termed "multiplets". These multiplets act as physical cross-links, which induces a reduction in chain mobility in the surrounding of the multiplets. As the ion content in an ionomer is increased, the size and/or the quantity of the multiplets increases. Once a sufficient quantity of multiplets is formed, the regions of restricted mobility begin to overlap. These large regions of closely spaced multiplets are termed clusters. The clusters may show phase-separated behavior, for example, a different T_g than that of the ion-poor regions ("matrix"). Therefore T_g increases with increasing ion content. As the T_g of the clusters is generally much higher than that of the matrix, a second T_g should be observed. On the other hand, as the ion content in the copolymer is low, the cluster volume is small compared to that of the backbone, which makes it difficult to detect the cluster's T_g by DSC. Usually only the T_g of the matrix is observed by this technique [5]. The morphology and mechanical properties of poly(MMA-*co*-sodium methacrylate) ionomers were recently investigated [10, 20–22]. It was found that the mechanical stability of the Ca salt ionomer is enhanced compared to that of the Na ionomer with the same ion content. To explain this behavior, it was suggested that the intermolecular interactions associated with the divalent Ca ion are stronger than the ion-pair interactions of the Na ionomer [10].

DSC experiments were performed on the pure homopolymers and the corresponding Na and Ca ionomers. T_g values higher than those of the homopolymers were clearly observed for the Na and Ca ionomers, even for an ion content of only 1.6 mol%. The values of T_g for the PMMA-based ionomers are reported in Fig. 6 versus the ion content. This plot shows three main features:

1. Na ionomers: the T_g increases with increasing ion content.
2. Ca ionomers: the T_g is always higher than that of the corresponding Na ionomer.
3. For a fixed ion content, the T_g of the Ca ionomers depends on their microstructure: the longer the ionic block, the lower the T_g value.

Feature 1 represents general properties observed for ionomers [5, 23]; feature 2 was found for various ionomer systems [5, 24, 25]. As for the third point, we can conclude that the micellar polymerization technique allows the synthesis of Ca ionomers with a T_g adjustable through the ionomer microstructure. This microstructure effect can be explained by the divalent nature of the Ca ions. If one considers an ionomer with isolated ionic units and carrying only one anionic charge per unit, the ionic sites must find an inter- or intramolecular counterpart, when neutralized with Ca^{2+} ions. This leads to an increased cross-linking and consequently to a higher T_g. In contrast, a blocky distribution of the ionic groups opens the possibility for the Ca ion to neutralize the charge within the same ionic block and fewer cross-links with other chains may be formed, resulting in a lower T_g. Such a model is illustrated in Fig. 7, showing the multiplet formation of isolated and blocky ionic groups between polymer chains.

As for Na ionomers, such an effect of the microstructure is not observed (at least for the ion content investigated) nor expected as Na^+ is monovalent, (Fig. 6).

The T_g is shown versus ion content for the PBA–NaA ionomers in Fig. 8. Owing to the high flexibility of the butyl side chain, the T_g is much lower than for PMMA. For the homopolymer, a T_g of −53.5 °C was measured, which is in good agreement with literature data (−54 °C [26]). As in the case of PMMA-based ionomers, a rise in the T_g with increasing ion content is also seen, although it is much less pronounced. The slope of T_g versus ion content is around 1.6 °C(mol%)$^{-1}$ of ions, in good agreement with results obtained from other BA-based ionomers: the slopes obtained for BAs with vinylpyrid-

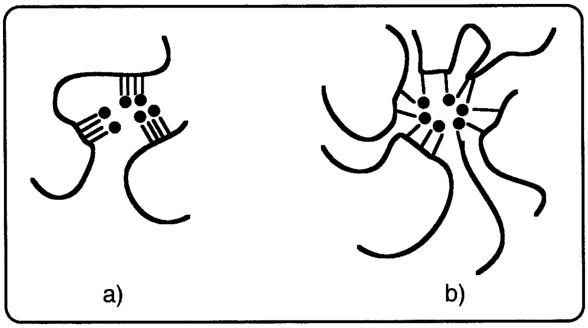

Fig. 7 Scheme of multiplet formation for blocky distributed ions (*a*) and for isolated ions (*b*)

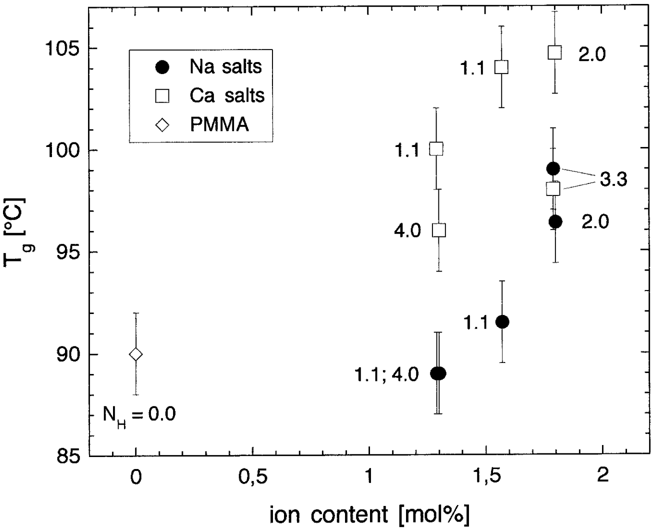

Fig. 6 Glass-transition temperature versus ion content for PMMA-based ionomers

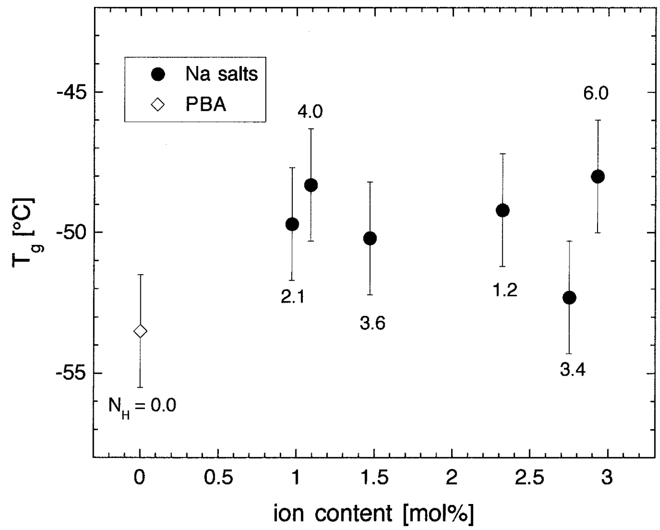

Fig. 8 Glass-transition temperature versus ion content for PBA–NaA ionomers

inium ionic groups [27] and for betaines [28] are 1 and 1.6 °C(mol%)$^{-1}$, respectively.

Conclusion

The present article is the first report on the synthesis of ionomers with randomly distributed ionic blocks of tunable length. This was achieved by means of free-radical copolymerization of a hydrophobic monomer (MMA or BA) with an ionic comonomer (NaA) in inverse AOT microemulsions. By varying the water/surfactant ratio, the number of ionic monomers per micelle, N_H, and therefore the ionic block length in the ionomer, can be tuned, keeping the hydrophobic/ionic monomer ratio constant.

The polymerization kinetics shows no difference between the homopolymerization and copolymerization reactions, nor dependence on the ionomer microstructure. AIBN is a more effective initiator than BPO, resulting in higher yields and faster kinetics.

The PMMA ionomers were directly obtained in their Na salt form and were subsequently transformed into Ca-based ionomers. The ionomers exhibit a narrow molecular-weight distribution with a weight-average molecular weight of around 40,000 for the PMMA samples and 60,000–100,000 for the BA samples. One limitation of the process is the compositional drift occurring during the reaction which leads to a somewhat higher ionic content than expected from the monomer feed composition.

In contrast to the Na ionomers, the DSC measurements performed on the Ca ionomers (based on PMMA) show a dependence of the T_g on N_H: a blocky distribution of the ionic units in the copolymer leads to lower T_g values than when the units are randomly distributed. This difference in behavior can be explained by the divalent nature of Ca^{2+} ions, which have the ability to form more interchain cross-links in the latter case.

Thus, we have demonstrated the feasibility of an inverse micellar copolymerization process for the synthesis of multiblock ionomers. Unique features of this technique are the direct synthetic access to ionomers and the tunability of the polymer microstructure, which influences the ionomer properties. Further work on systems containing higher ionic contents and longer ionic blocks should allow ionomers with enhanced microstructure effects to be obtained.

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References

1. Candau F, Selb J (1999) Adv Colloid Interface Sci 79:149–172, and references therein
2. Volpert E, Selb J, Candau F (1996) Macromolecules 29:1452
3. Jimenez-Regalado E, Selb J, Candau F (1999) Macromolecules 32:8580
4. Eisenberg A, Hird B, Moore RB (1990) Macromolecules 23:4098
5. Eisenberg A, Kim JS (1998) Introduction to ionomers. Wiley, New York
6. Vaskova V, Juranicova V, Barton J (1990) Makromol Chem 191:717
7. Vaskova V, Juranicova V, Barton J (1991) Makromol Chem 192:989
8. Nuno-Donlucas SM, Diaz-Najera LM, Gonzalez-Nunez R, Martinez-Rico MA, Puig JE (1997) J Appl Polym Sci 66:879
9. Rogers J, Winsor PA (1969) J Colloid Interface Sci 30:247
10. Ma X, Sauer JA, Hara M (1995) Macromolecules 28:3953
11. Ekwall P, Mandel L, Fontell K (1970) J Colloid Interface Sci 33:215
12. Zulauf M, Eicke HF (1979) J Phys Chem 83:480
13. Candau F, Leong YS, Pouyet G, Candau S (1984) J Colloid Interface Sci 110:167
14. Frank SG, Zografi G (1969) J Colloid Interface Sci 29:27
15. Lang J, Jada A, Malliaris A (1988) J Phys Chem 92:1946
16. Day RA, Robinson BH, Clarke CHR, Doherty JV (1979) J Chem Soc Faraday Trans I 75:132
17. Brandrup J, Immergut E (1989) Polymer handbook. Wiley, New York, pp II-4, II-32
18. Schulz GV, Henrici-Olivé G, Olivé S (1959) Makromol Chem 31:88
19. Biggs S, Hill A, Selb J, Candau F (1992) J Phys Chem 96:1505
20. Ma X, Sauer JA, Hara M (1995) Macromolecules 28:5526
21. Nah YH, Kim JS, Jo BW, Kim J, Lee Y (1999) Polym Bull 42:213
22. Kim JS, Nah YH, Jarng SS, Kim W, Lee Y, Kim YW (2000) Polymer 41:3099
23. Eisenberg A, King M (1977) Polymer physics, vol 2. Ion-containing polymers. Academic, New York
24. Matsuura H, Eisenberg A (1976) J Polym Sci Polym Phys Ed 14:1201
25. Eisenberg A, Farb H, Cool LG (1966) J Polym Sci Part A-2 4:855
26. Brandrup J, Immergut E (1989) Polymer handbook. Wiley, New York, pp VI-214
27. Duchesne D, Eisenberg A (1990) Can J Chem 68:1228
28. Ehrmann M, Mathis A, Meurer B, Scheer M, Galin JC (1992) Macromolecules 25:2253