values that are presented in Table II establishes the validity of the contrast-matching technique and verifies the earlier similar measurements on sodium salts.[10]

The most significant feature of the results is that the radius of gyration is remarkably constant. Only small variation in comparison to the statistical error is observed over the entire range of degree of sulfonation, concentration, and counterion that has been studied in these experiments. This may be contrasted with the knowledge that neutron and light scattering shows these ionomers to form aggregates in this range of concentration and that the viscosity data in Figure 1 show a clear change from depression of viscosity of augmented viscosity that has hitherto been associated with the transition from a collapsed intramolecular association of ionic groups at low concentrations to intermolecular association at higher concentrations.

The free acid ionomer does not associate strongly in tetrahydrofuran; a small but significant trend of expansion with increasing ionic strength is observed in these measurements. This systematic variation is perhaps best attributed to steric effects of solvated acid groups and is consistent with the results of preliminary light-scattering experiments.

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Effects of Internal Plasticization on Ion Aggregation in a Styrene Ionomer

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ABSTRACT: A copolymer of styrene with 7 mol % methacrylic acid was alkylated with 1-decene in a Friedel–Crafts-type reaction. Both glass transition temperatures associated with the matrix and with the clusters were shifted to lower temperatures with increasing alkylation, and the modulus at the rubberlike inflection point dropped by over an order of magnitude. It was shown that ion clustering was enhanced at alkylation levels of up to ca. 20 mol %, compared with the parent ionomer. At higher degrees of alkylation, however, the alkyl chains strongly disrupted the ionic association. Even though some clustering effects were still observed in the loss tangent–temperature curves, the large drop in the rubberlike modulus showed that the influence of the clusters on the rheological properties of the polymer was not significant.

Introduction

For over 2 decades, the field of ion-containing polymers has been an area of growing interest. This is demonstrated by a number of books,[1,2] reviews,[3] and recent symposia[4] on the topic, as well as by the increasing number of ionomers available commercially, with their many current and potential applications.[5] The interest in these materials is justified by the sometimes drastic changes observed in the bulk properties of the polymers, as a consequence of the introduction of low concentrations (up to ca. 15 mol %) of ionic units. The modifications in the properties of anionic materials may be explained on the basis of phase separation,[6] whereby the ions tend to aggregate to form ion-rich regions in the polymer matrix. The existence of two types of aggregates, namely multiplets and clusters, has been proposed.[7]

The behavior of cationomers, however, is very different from that of anionic materials: previous studies on polystyrene-based *N*-alkyl-4-vinylpyridinium halide systems have shown no evidence of clustering;[8] nevertheless, earlier studies on polybutadiene-based cationomers do show some characteristics of clustered systems at comparable ionic concentrations.[9] Butyl acrylate and plasticized ethyl acrylate cationomers also show similar effects.[10]

The differences observed in anionic systems compared with cationic systems of similar structure illustrate one of the many structural factors known to affect ion aggregation, namely, in this case, the type of ion used. Some of the other factors involved are the placement of the ions

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relative to the chain,[11] the type of counterion used,[12] and the degree of neutralization.[13] Another example of a parameter affecting ion aggregation is the matrix glass transition temperature of the polymer, sometimes related to the stiffness of the chain. Thus, some high-temperature polymers do not exhibit clustering,[14] while a lowering of the T_g induces cluster formation in other systems.[10]

Some effects of low molecular weight diluents in ionomers, which are relevant to this study, have been explored by Bazuin and Eisenberg.[15] In this case, the effects on the mechanical behavior of two diluents, one nonpolar (diethylbenzene, DEB) and the other polar and hydrogen-bonded (glycerol), were observed in a carboxylated styrene ionomer and in a sulfonated styrene ionomer. Diethylbenzene was found to act as a conventional nonpolar plasticizer, the Fox equation[16] being followed quite closely. Furthermore, the slope steepness of the modulus–temperature plot in the glass transition region decreased, and both the matrix and the ionic loss tangent peaks broadened and shifted to lower temperatures with increasing DEB content. The modulus of the ion-related rubberlike plateau observed in the bulk material decreased in height and was shifted down on the temperature scale, eventually to disappear at higher DEB contents.

The original aim of this work was to explore the effect of the variation of the glass transition temperature on ionic aggregation in a carboxylated polystyrene-based ionomer. In contrast to previous work, however, this T_g variation was to be accomplished via internal plasticization, in the absence of small molecules. The lowering of the T_g, combined with the low polarity of the product, would, intuitively, have been expected to favor clustering. However, it was found that, although some clustering enhancement was observed at low levels of substitution, high levels had a strong disruptive effect on large-scale ionic aggregation. These phenomena are the subject of the present work. SAXS experiments on the alkylated materials are currently in progress and will be reported subsequently.

For the sake of completeness, it should be noted that plasticization of styrene ionomers has also been achieved with the help of *n*-alkyl-substituted amines used as counterions.[17] The approach used in this work is, however, significantly different, in that the polymer matrix is plasticized in a nonspecific manner, rather than only at the ionic sites. Another consequence of this is that the ion content does not vary with the plasticization level.

Experimental Section

A copolymer of styrene–methacrylic acid (PS–0.07 MAA of molecular weight ca. 10^5 g/mol) was prepared by using a bulk polymerization technique already reported.[18]

The methacrylic acid content of the copolymers was determined by titration of 0.4-g samples in 90/10 v/v benzene–methanol as a solvent. The solutions were titrated to the phenolphthalein end point with methanolic 0.05 N NaOH, and a blank correction was included in the calculations.

The following alkylation procedure was developed to graft alkyl chains onto the aromatic rings of styrene. The alkylating agent, 1-decene (Aldrich), was previously purified by distillation under reduced pressure (bp 63–64 °C/12 mmHg). All other reagents and solvents were reagent grade and used as received from the suppliers. The copolymer (5 g, 45.2 mmol of styrene units) was dissolved in 125 mL of a 25/10 v/v carbon disulfide (A&C American Chemicals)/1-nitropropane (Aldrich) mixture contained in a round-bottomed flask fitted with a refluxing condenser. Decene (20 mL, 106 mmol) was added to the flask, and the solution was warmed to near its boiling point. A solution of 6 g (45 mmol) of anhydrous aluminum chloride (Anachemia) in 50 mL of the carbon disulfide–nitropropane solvent was then added with vigorous stirring to the polymer solution. The condenser was fitted with a drying tube, to avoid the introduction of excessive amounts of moisture into the system. The reaction mixture was refluxed for variable amounts of time, to produce degrees of alkylation of up to ca. 100 mol % based on the styrene rings.

The volume of solvent in the reaction flask was then reduced to ca. 100 mL on a rotary evaporator, and the polymer was precipitated with vigorous stirring in 1 L of methanol. Sample purification was achieved by redissolving the air-dried polymer in a boiling mixture of 500 mL of chlorobenzene (Anachemia) and 50 mL of 2-propanol (A&C American Chemicals) with stirring, followed by the addition of 25 mL of distilled water and overnight refluxing. The aqueous phase was then eliminated, and the organic solution washed 5 times with 150-mL portions of distilled water. The amount of solvent was again reduced to about 100 mL, and the polymer was precipitated in 1 L of methanol. The samples were finally dried for 2–3 days in a vacuum oven at 150 °C. The degree of substitution evaluated by NMR spectroscopy was used to calculate expected sample weight increases to allow yield calculations. Experimental yields of purified alkylated polymers were typically 80–90% of the theoretical value.

Samples with alkylation levels of up to 103 mol % (based on the styrene rings) were obtained in this manner. Slightly modified reaction conditions were used to produce alkylated ionomers in the 0–30% range with better control on the reaction time. In this case, 250 mL and 100 mL of the CS_2/nitropropane solvent were used for the polymer and aluminum chloride, respectively, yielding approximately halved concentrations for all reagents.

Characterization. The degree of alkylation was determined by two independent methods. The first technique involved the determination of the equivalent weight (EW) of the material by standard acid–base titration. Assuming that none of the carboxylic acid groups of the copolymer were affected in the Friedel–Crafts reaction, the degree of alkylation (x) could be calculated from the equivalent weight (EW) determined by titration of the copolymer as

$$x = \frac{\text{EW}-1470\ \text{g}\cdot\text{mol}^{-1}}{3333-1470\ \text{g}\cdot\text{mol}^{-1}} \tag{1}$$

where the constants 1470 and 3333 g·mol^{-1} represent the equivalent weights of nonalkylated and 100% alkylated PS–0.07 MAA, respectively.

The second method used to determine the alkylation level was Fourier transform ^{1}H NMR spectroscopy. All NMR spectra were recorded on a Varian XL-200 spectrometer at 20 °C. A mixture of 90/10 v/v of deuterated benzene and deuterated methanol was used as a solvent for all samples. A series of 32 transients was recorded for each spectrum. The alkylation level was in this case evaluated from the ratio of the integrated areas of the peaks for the aromatic (δ = 6.2–7.6 ppm) and the aliphatic protons (δ = 0.5–2.5 ppm), respectively.

Mechanical Measurements. The dynamic mechanical properties of the samples were determined as a function of temperature using an inverted torsional pendulum described elsewhere.[19] The system used a PDP-11/03 microcomputer for signal acquisition and analysis.

The samples used in the instrument had approximate dimensions of 1.7 × 0.6 × 0.2 cm^3 and were molded from 1 g of predried material (1 week in vacuo at 150 °C) by compression at 50–100 °C above matrix T_g. Pressure was maintained at up to 15 MPa for 15–20 min. The mold was then left to cool slowly on the press to below T_g, and the sample was taken out. The molded sample was stored in a vacuum oven at a temperature close to its matrix T_g or used immediately in the instrument.

Software was developed to evaluate the peak maxima and the inflection points in the modulus–temperature curves.[20]

Results and Discussion

Synthesis. Decene was selected as the alkylating agent because a minimum is observed at that value in a plot of the glass transition temperature versus chain length in the analogous poly(4-alkylstyrene) series, at T_g = −65 °C.[21] It should consequently be possible to achieve a large T_g depression with a C_{10} unit, while avoiding complications due to side-chain crystallization, which is apparently significant for side chains longer than about 12–14 carbon atoms. The

Table I
Comparison of the Results Obtained for the Determination of the Alkylation Level by NMR and by Titration

titration, mol %	NMR, mol %	titration, mol %	NMR, mol %
10 ± 2	7.5 ± 0.4	52 ± 3	53 ± 3
18 ± 2	15.0 ± 0.8	78 ± 4	70 ± 4
36 ± 3	32 ± 2	102 ± 5	104 ± 5

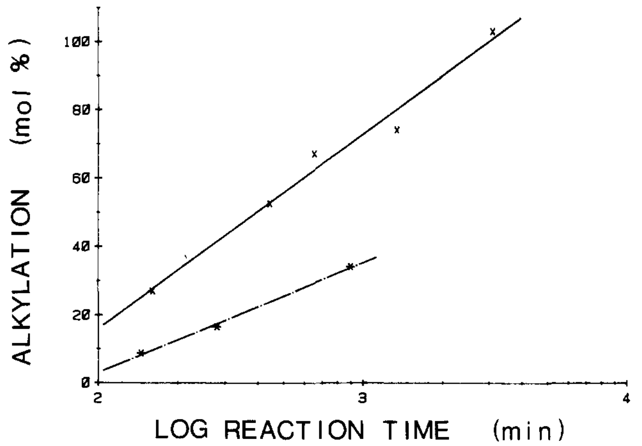

Figure 1. Conversion curves for the Friedel–Crafts alkylation of the PS–0.07 MAA copolymer with 1-decene in the concentrated (×) and dilute (*) reaction conditions described in the text.

product obtained in the reaction has the advantage of being reasonably well characterized for the purpose of this study. The reaction conditions used, as well as the steric hindrance caused by the backbone, are expected to favor predominantly the formation of the para isomer.[22] As is generally the case with Friedel–Crafts reactions, the cationic alkyl species generated in the reaction are likely to rearrange, via hydride migration, thus producing isomers with attachment points at C-2 to C-5 on the alkyl chain. The presence of a few different isomers is considered an advantage here, since this factor should further contribute to the inhibition of side-chain crystallization. The absence, within experimental error limits, of further rearrangements such as methyl migrations, is demonstrated by the NMR results. The evaluation of the degree of alkylation from the ratio of the integrated areas of the aromatic protons (δ = 6.2–7.6 ppm) to the area of all the aliphatic protons (δ = 0.5–2.5 ppm) or only the methyl protons (δ = 0.95 ppm) in the spectrum, respectively, gives the same results.

The degrees of alkylation obtained from the equivalent weight determinations and those from NMR are summarized in Table I. It can be seen that neither technique gives consistently higher or lower results; the variations, therefore, are most likely due only to random errors. It should be noted that, since the method involving titrations relies on the difference between the equivalent weight of the alkylated and the nonalkylated materials, its precision is somewhat limited at the lower alkylation levels. An error of ca. 2 drops or 0.05 mL can be assumed in the titrations, due to the relatively diffuse end point observed in titrations in organic solvents. Since titrant (0.05 N NaOH) volumes of typically 3–5 mL were used for 0.4-g samples, relative errors of ca. 1–1.7% were obtained on the individual measurements. When the EW of the nonalkylated polymer is subtracted from the EW of the alkylated material, however, the absolute errors add up, yielding rather larger relative errors ranging from about 5% (102% alkylated) to 15% (10% alkylated). The NMR technique is expected to give more reliable results than the equivalent weight approach at the lower alkyl contents. The accuracy of the values obtained in this manner (considering spectrum phasing errors) is expected to be of the order of about 5% of the values determined. Consequently, the alkylation levels used in the calibration curves for the alkylation reaction (Figure 1), and reported subsequently, are the average of the two determinations.

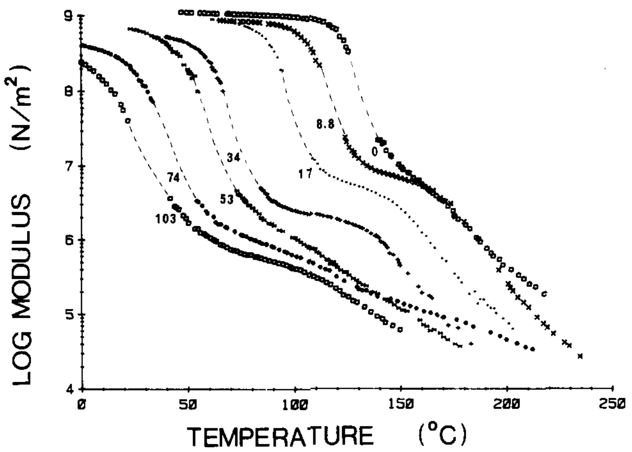

Figure 2. Storage modulus curves for the PS–0.07 MAA–Na system alkylated with 1-decene. The curves are identified by the mole percent of styrene rings with alkyl chains grafted on them.

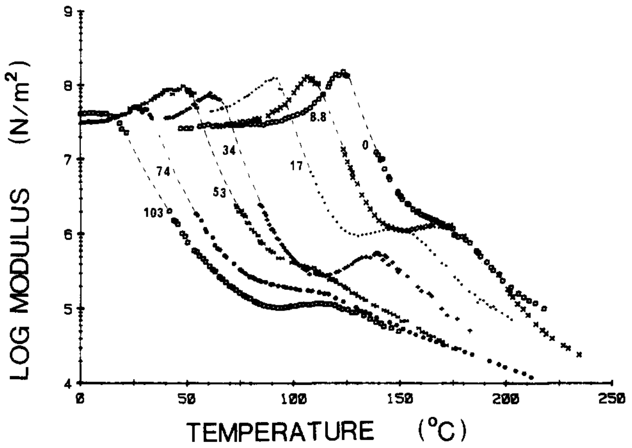

Figure 3. Loss modulus curves for the alkylated PS–0.07 MAA–Na ionomers.

Two lines (Figure 1) were obtained to relate the degree of alkylation of the copolymers to the reaction time. The curve with the lower slope refers to samples prepared under the more dilute reaction conditions. This modified procedure was preferred for the samples with the lower alkyl contents, to maintain a better control on the reaction times involved.

The fact that the plot of the degree of alkylation against the logarithm of the reaction time displays relatively good linearity (correlation coefficient $r^2 = 0.990$) does not seem to have any theoretical significance. The reaction was found to obey pseudo-first-order kinetics in the concentration of polymer, for degrees of alkylation of up to 67 mol %. The rate constants were determined as $(7.6 \pm 0.4) \times 10^{-6}$ and $(3.1 \pm 0.1) \times 10^{-5}$ s^{-1} for the dilute and the concentrated solutions, respectively. The values of the uncertainities (from linear regression analysis), however, should be regarded with much caution, because of the very limited number of points available for the analysis (three in each case).

Mechanical Properties. The storage modulus, loss modulus, and loss tangent curves for the sodium-neutralized styrene–methacrylic acid ionomers (PS–0.07 MAA–Na) at degrees of alkylation varying from 0 to 103 mol % are displayed in Figures 2–4. The useful infor-

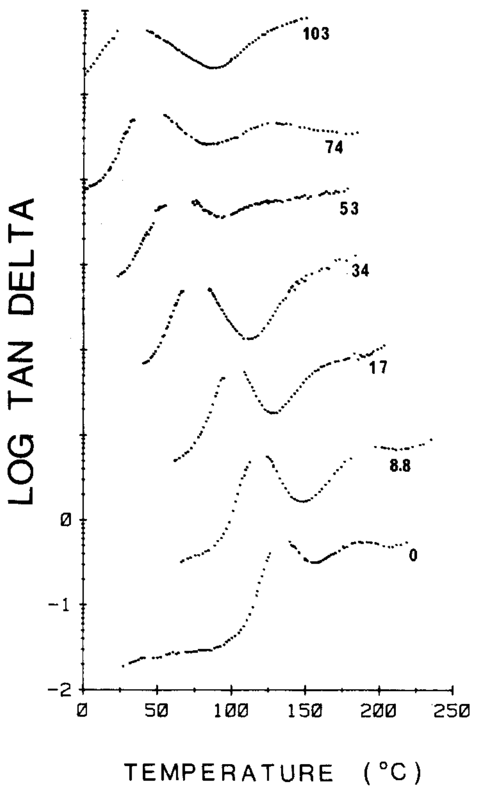

Figure 4. Loss tangent curves for the ionomers of Figure 2. Each curve is shifted up by an order of magnitude with respect to the previous one, for improved clarity.

Table II
Summary of the Results Obtained from the Numerical Analysis of the Loss Tangent and Modulus–Temperature Curves of the Alkylated Ionomers

alkylation, mol %	matrix		"rubbery" inflection pt		clusters	
	T_{g1}, °C	$W_{1/2}$, °C	T_{in}, °C	G'_{in}, MPa	T_{g2}, °C	$W_{1/2}$, °C
0	133	22	158	6.2	186	30
8.8	119	23	146	7.3	191	38
17	101	22	125	5.8	166	37
34	75	25	107	2.3	148	39
74	44	31	87	0.87	128	45
103	33	42	85	0.57	127	36

mation extracted from these curves with the help of the data analysis program is summarized in Table II. The table lists, for each sample, the matrix tan δ peak position (T_{g1}) and its width at half-height ($W_{1/2}$), the value of the rubberlike inflection modulus (G'_{in}) and temperature (T_{in}), and the cluster peak position (T_{g2}) and width at half-height ($W_{1/2}$).

The width of the glassy to rubbery transition zone in the G' curves (Figure 2) increases with the alkylation level. This parallels the observation by Bazuin and Eisenberg[15] for ionomers with low molecular weight diluents. The phenomenon is quantified by the width at half-height for the matrix peaks (Table II, third column). A three-dimensional damped Debye lattice model was used by Chapoy and Tobolsky[23] and by Aklonis and Rele[24] to explain the widening of the transition region in plasticized samples. In this model, the diluent reduces intermolecular interactions and progressively destroys the three-dimensional torsional oscillator lattice, thereby reducing the steepness of the slope in the transition region.

The rubberlike plateau in the G′–temperature curves is initially extended as the plasticizer content increases and the T_g of the material goes down; however, it becomes less clearly defined at the higher (74 and 103 mol %) alkylation levels.

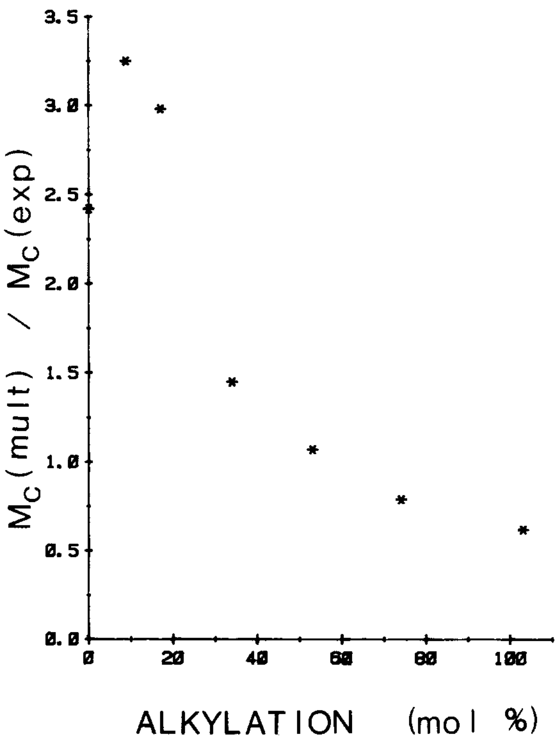

Figure 5. Extent of aggregation observed in the alkylated ionomers expressed as the ratio of calculated M_c for multiplet-type interactions to experimental M_c.

The shifts in the temperatures of the two maxima in the tan δ curves are given in Table II. It can be seen that, at low degrees of alkylation, the behavior of the cluster T_g is very different from the matrix T_g. The matrix T_g decreases monotonically with plasticizer content. The cluster T_g, on the contrary, increases initially with respect to the parent ionomer. The point for the cluster T_g of the 8.8% alkylated ionomer is of particular interest here. The errors involved in determining the positions of the maxima with the help of the data-fitting and base-line subtraction routines are expected to be of the order of 1 °C for the sharp matrix peak and 2–3 °C for the cluster peak, depending on its shape. Therefore, it seems unlikely that this particular point can be attributed to experimental error but rather represents the manifestation of an enhanced state of clustering. These results are consistent with the observation by Duchesne and Eisenberg[10] that decreasing the matrix T_g from an ethyl acrylate (T_g = −24 °C) to a butyl acrylate matrix (T_g = −54 °C)[21] induced cluster formation in vinylpyridinium ionomers; similar results were obtained when the ethyl acrylate ionomers were plasticized with dimethyl malonate.

The validity of the present findings is further reinforced by the evaluation of the apparent average molecular weight between cross-links from the rubberlike inflection point of the G'–temperature curve ($G_{in} = \rho R T_{in}/M_c$) for the different samples. A measure of the extent of aggregation can be obtained by comparing the experimentally determined M_c to the "stoichiometric" M_c calculated for strictly multiplet-type ionic interactions and is equal to the equivalent weight of the sample. This is presented graphically in Figure 5 as a ratio of the two values. The 8.8% and 17% samples have an M_c ratio clearly higher than the parent ionomer, revealing once again an increased state of clustering. It is believed that the consistency of the data presented in Table II and Figure 5 points to an enhanced state of large-scale ionic aggregation (clusters) at the lower alkylation levels. A possible explanation for this phenomenon could be an increase in the packing efficiency of the ions, as a result of the increased mobility of the polymer backbone. At alkylation levels above 50–60 mol %, however, the ionic interactions fall below the statistical multiplet-type level [$M_c(\text{mult})/M_c(\text{exp}) < 1$], pointing to the highly disruptive nature of the grafted alkyl chains. It seems likely that the bulkiness of the grafted alkyl chains significantly hinders the approach of ion pairs at high concentrations, thereby reducing the extent of interactions and the driving force for large-scale aggregation. The decrease in the cluster T_g at the higher alkylation levels could be explained in the following manner. Measurements on phase-separated styrene–dimethylsiloxane block copolymers[25] have shown that, for short styrene block lengths, the T_g's of the styrene phase were lower than for polystyrene homopolymers of comparable molecular weights. Two distinct possibilities were suggested to explain these results, namely the mixing of the two phases at the interface and the existence of strong dynamic interactions at the microphase interface ("soft-wall" effect). The first possibility seems less likely in the case of ionomers, since the "hard" phase (clusters) is highly ionic in nature. It is also conceivable that the plasticizer becomes incorporated in the clusters and lowers the T_g by that mechanism. This seems unlikely, however, because of the very different solubility characteristics of the materials. Furthermore, as can be seen in Figure 4, the height of the loss tangent peaks due to the clusters is not a function of the plasticizer content.

Conclusions

It was shown that the lowering of the matrix T_g of carboxylated ionomeric systems at low levels of internal plasticization leads to increased ionic aggregation. In this particular case, clustering enhancement was observed, with respect to the nonalkylated parent ionomer, for 1-decene contents of up to 15–20 mol %. At much higher alkylation levels, however, the large grafted alkyl chains apparently reduced the aggregation state to mostly multiplet-type interactions.

A reaction was suggested to graft 1-decene onto the rings of aromatic homopolymers and carboxylated copolymers in a Friedel–Crafts-type reaction, in order to lower the T_g of the samples. The kinetics of the reaction were briefly examined.

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