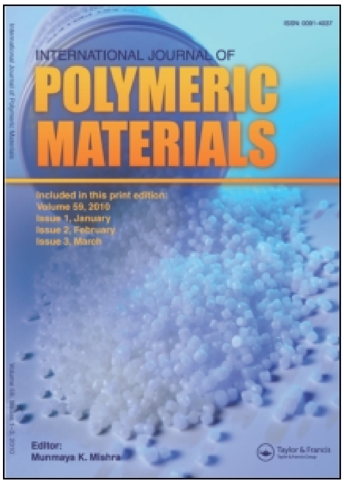


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Dynamic Melt Rheological Properties of Ionomers Based on Poly(Ethylene-*co*-Acrylic Acid) and Poly(Ethylene-*co*-Methacrylic Acid)

Thomas Kurian[a]; Mihoko Nishio[b]; Akihiro Nishioka[a]; Tatsuhiro Takahashi[a]; Kiyohito Koyama[a]
[a] Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, India [b] Department of Polymer Science and Engineering, Yamagata University, Yonezawa, Japan

To cite this Article Kurian, Thomas , Nishio, Mihoko , Nishioka, Akihiro , Takahashi, Tatsuhiro and Koyama, Kiyohito(2007) 'Dynamic Melt Rheological Properties of Ionomers Based on Poly(Ethylene-*co*-Acrylic Acid) and Poly(Ethylene-*co*-Methacrylic Acid)', International Journal of Polymeric Materials, 56: 2, 135 — 145

To link to this Article: DOI: 10.1080/00914030600754842

URL: http://dx.doi.org/10.1080/00914030600754842

International Journal of Polymeric Materials, 56:135–145, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600754842

Dynamic Melt Rheological Properties of Ionomers Based on Poly(Ethylene-*co*-Acrylic Acid) and Poly(Ethylene-*co*-Methacrylic Acid)

Thomas Kurian
Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, India

Mihoko Nishio
Akihiro Nishioka
Tatsuhiro Takahashi
Kiyohito Koyama
Department of Polymer Science and Engineering, Yamagata University, Yonezawa, Japan

The high temperature stability, and the dynamic melt rheological properties of poly(ethylene-co-acrylic acid) (EAA), zinc salt of EAA, and sodium salt of EAA were evaluated in the molten state over broad ranges of shear rates and temperatures using ARES (Rheometrics). The master curves of G' *and* G'' *as a function of angular frequency* (ω) *were constructed for each material. The influence of ionic groups on the storage modulus* (G')*, loss modulus* (G'')*, complex viscosity* (η^*)*, and flow activation energy* (E_a) *were analyzed. The results of EAA based ionomers are discussed with those of the ionomers based on poly(ethylene-co-methacrylic acid) (EMAA). The linear visco-elastic spectra, and flow activation energies of the two series of ionomers show differences.*

Keywords: dynamic, ionomer, poly(ethylene-*co*-acrylic acid), poly(ethylene-*co*-methacrylic acid), viscosity

Received 31 March 2006; in final form 10 April 2006.

The authors express their special thanks to Mr. Y. Yamamoto and Mr. T. Watanabe of Mistui-DuPont Polychemicals Co., Ltd., Japan for molecular analysis and helpful discussions. This work was financially supported by the Japan Society for Promotion of Science (JSPS Postdoctoral Fellowship No. P 01778 to Thomas Kurian).

Address correspondence to Thomas Kurian, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682 022, India. E-mail: tkurian@cusat.ac.in

INTRODUCTION

Ionomers are polymers containing low levels of ionic groups [1]. Because of the interionic electrostatic forces, as well as the high degree of thermodynamic incompatibility between the polar ionic groups and the nonpolar hydrocarbon polymer matrix, ionic groups aggregate in the bulk and form physical crosslinks [2–3]. The ionic crosslinks are thermoreversible, particularly under shear, by ion hopping mechanism, which allows the viscosity of ionomers to be decreased to such a level that they could be easily processed [4–5]. Ionomers have emerged as important industrial polymers, because of their improved mechanical properties as compared to the base materials [6]. The properties of ionomers are dependent on the type of polymer backbone, ionic content, type of cation, and the degree of neutralization [6–7].

The ionomers based on Poly(ethylene-*co*-methacrylic acid) (EMAA) are the most widely used ionomers. The presence of ionic crosslinks imparts a profound influence on the flow properties of ionomer melts. The melt-flow mechanism of ionomers remains poorly understood. Takahashi et al. [8] have investigated the effects of ionic interactions on the uniaxial extensional flow of EMAA, and its metal salts. The melt rheology of poly (ethylene-*co*-acrylic acid) (EAA) based ionomers has not yet been extensively investigated. This article reports the results of investigations on the high temperature stability, and the dynamic melt rheological behavior of EAA, zinc salt of EAA, and sodium salt of EAA evaluated in the molten state over broad ranges of shear rates, and temperatures. The dynamic melt rheological properties of EAA-based ionomers are compared with those of EMAA-based ionomers.

EXPERIMENTAL

Materials

The polymers used in this study were (i) EAA ($M_n = 21247$, $M_w = 215508$, acrylic acid content = 15 wt% (6.4 mol%)), (ii) zinc salt of EAA abbreviated as EAAZn-63 (level of neutralization = 63%), (iii) sodium salt of EAA abbreviated as EAANa-58 (level of neutralization = 58%), (iv) EMAA ($M_n = 19200$, $M_w = 94500$, methacrylic acid content = 15.0 wt% (5.4 mol%)), (v) zinc salt of EMAA abbreviated as EMAAZn-59 (level of neutralization = 59%), and (vi) sodium salt of EMAA abbreviated as EMAANa-54 (level of neutralization = 54%). All the polymers were provided by Mistui-DuPont Polychemicals, Japan. The polymer samples were dried for one week before compression molding, and the disk shaped test pieces, of 2 mm thickness and 25 mm diameter, were further dried for three days under vacuum at 80°C before measurements to eliminate the effect of moisture.

Measurement of Dynamic Melt Rheological Properties

The dynamic melt rheological properties of the samples were determined using the compression-molded disks on a dynamic mechanical spectrometer (ARES, Rheometric Scientific) using 25 mm parallel plate fixtures operating under RSI Orchestrator software for automatic equipment control, data acquisition, and analysis. The sample compartment was continuously blanketed with nitrogen. Nitrogen temperature was used to control the sample temperature. Dynamic measurements were performed within the linear viscoelastic (LVE) region obtained by dynamic strain sweep tests. The samples were examined after the experiments to ensure their uniformity and absence of edge instability. The reproducibility of the measured parameters was tested with at least three repetitions using samples of the same composition. The high temperature stability of the materials was evaluated by repeating the dynamic frequency measurements three times at 180°C using the same test piece.

RESULTS AND DISCUSSION

Stability of EAA-Based Ionomers

The variation of storage modulus G′, and loss modulus G″ of EAA as a function of angular frequency (ω) at 180°C is shown in Figure 1(a). On repeating the measurements three times using the same sample the storage modulus and the loss modulus values remain almost constant. Figures 1(b) and (c) show the results of similar measurements using EAAZn-63, and EAANa-58. It was observed that the storage modulus and the loss modulus values remain unchanged in the case of the EAA-based ionomers too, on repeating the measurements up to three times. The total duration for which each test piece was kept at 180°C during the evaluation of stability was 30 min. The results indicate that the EAA, and the ionomers based on EAA, are stable under the test conditions used in the present investigations.

Melt Flow Behavior of EAA-Based Ionomers

Figure 2 shows the time-temperature master curve of storage modulus G′ and loss modulus G″ as a function of angular frequency (ω)

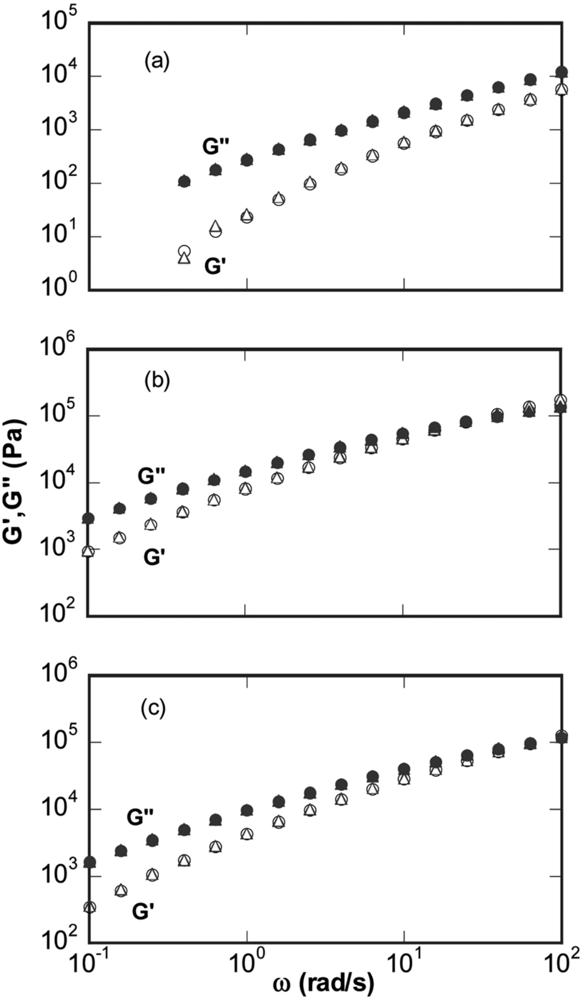


FIGURE 1 The storage modulus (G′) and loss modulus (G″), respectively, of the first test (○, ●), and third test (△, ▲) from the results of stability evaluation at 180°C by three cycles of repeated dynamic frequency measurements of: (a) EAA, (b) EAAZn-63, and (c) EAANa-58.

constructed for EAA at 120, 140, and 160°C. The reference temperature was 120°C. The graphical presentation clearly demonstrates that the super position principle is applicable, and the material is stable under the test conditions.

The curves obtained for EAA at the higher temperatures were horizontally shifted for construction of the super master curve. The

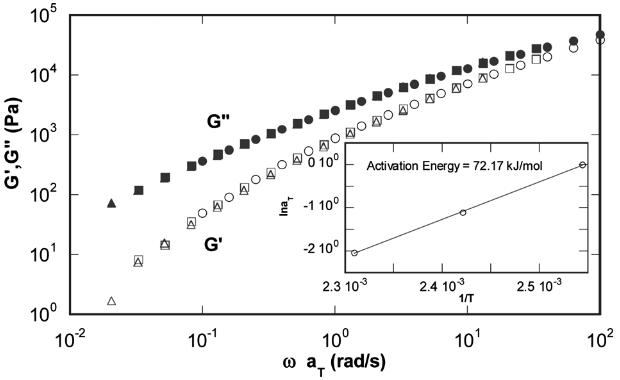


FIGURE 2 Time-temperature master-curves of storage modulus (G′) and loss modulus (G″), respectively, of EAA at: 120°C (○, ●), 140°C (□, ■), and 160°C (△, ▲).

time-temperature shift factors (a_T) at 120,140, and 160°C were 1.0, 0.33, and 0.13.

The temperature dependence of the shift factors (a_T) could be described by the Arrhenius relation [9]:

$$\ln a_T = \frac{E_a}{R((1/T) - (1/T_0))} \tag{1}$$

where R is the universal gas constant, and E_a is the flow activation energy. On plotting $\ln a_T$ versus 1/T, the flow activation energy (E_a) was found to be 72.1 kJ/mol for the base EAA (Table 1).

The time-temperature master curves of EAAZn-63 are shown in Figure 3. The time temperature shift factors (a_T) for the ionomer at 140, 160, and 180°C were 1.0, 0.385, and 0.135. The flow activation energy calculated from the Arrhenius plot was 77.7 kJ/mol (Table 1).

In the case of polyethylene both long and short chain branches have been known to lead to higher flow activation energies [10–11]. The

TABLE 1 Flow Activation Energies

Material	E_a (kJ/mole)
EAA	72.1
EAAZn-63	77.7
EAANa-58	103.2
EMAA	70.4
EMAAZn-59	105.1
EMAANa-54	95.9

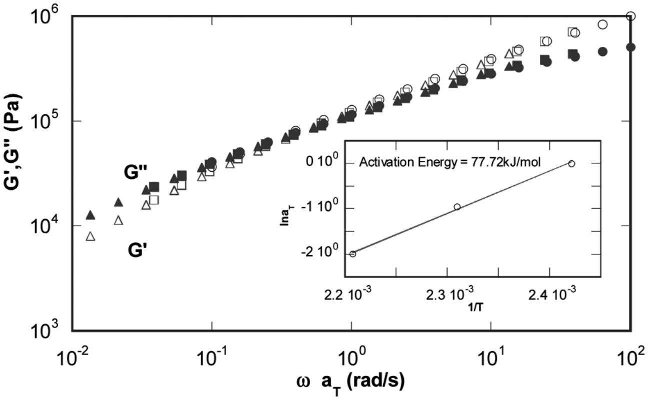


FIGURE 3 Time-temperature master-curves of storage modulus (G′), and loss modulus (G″), respectively, of EAAZn-63 at: 140℃ (○, ●), 160℃ (□, ■), and 180℃ (△, ▲).

enhancement of flow activation energies in polymers on incorporation of ionic groups is presumably due to the flow resistance imparted by the ionic domains [12]. Earlier reports suggest a linear relationship between the content of ionic groups and the flow activation energies in the case of sulfonated PET and sulfonated styrene-butadiene rubber [12–13].

The master curves of EAANa-58 are shown in Figure 4. The time-temperature shift factors (a_T) for the ionomer at 140, 160, and 180℃

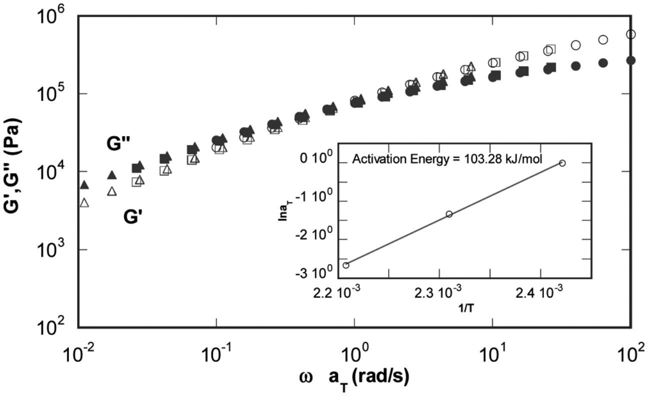


FIGURE 4 Time-temperature master-curves of storage modulus (G′) and loss modulus (G″), respectively, of EAANa-58 at: 140℃ (○, ●), 160℃ (□, ■), and 180℃ (△, ▲).

TABLE 2 Complex Viscosity Values from Time-Temperature Master Curves

Material	η^* (Pa.s) at $\omega = 10^{-1}$ (rad/s)	η^* (Pa.s) at $\omega = 10^{0}$ (rad/s)	η^* (Pa.s) at $\omega = 10^{1}$ (rad/s)
EAA	1.22×10^3	1.06×10^3	6.90×10^2
EAAZn-63	4.97×10^5	1.62×10^5	4.81×10^4
EAANa-58	3.23×10^5	1.17×10^5	2.99×10^4
EMAA	1.71×10^3	1.48×10^3	9.40×10^2
EMAAZn-59	7.87×10^5	2.41×10^5	5.98×10^4
EMAANa-54	1.30×10^5	5.91×10^4	1.88×10^4

were 1.0, 0.265, and 0.070. The flow activation energy (Table 1) in the case of EAANa-58 was 103.2 kJ/mole.

A comparison of the dynamic melt rheological properties of EAA, with its zinc ionomer, and sodium ionomer shows that the flow activation energies (Table 1) are in the order EAA < EAAZn-63 < EAANa-58, whereas the melt viscosities (Table 2) show the order EAA < EAANa-58 < EAAZn-63.

Melt Flow Behavior of EMAA-Based Ionomers

The activation energies of EMAA series ionomers and their base materials are also shown in Table 1. The dynamic shear measurements of EMAA were carried out at 130, 140, and 150°C. The shift factors (a_T) for the test temperatures were found to be 1.0, 0.59, and 0.37. The flow activation energy of the parent unfunctionalised EMAA was 70.4 kJ/mole.

The dynamic shear measurements of EMAA-based ionomers were carried out at 140, 160, and 180°C. The time-temperature shift factors (a_T) for the aforementioned test temperatures in the case of EMAAZn-59 and EMAANa-54 were 1.00, 0.24, and 0.067, and 1.00, 0.25, and 0.085, respectively. The super position principle was applicable in the case of both ionomers.

It was possible to express the temperature dependence of shift factors (a_T) with the Arrhenius equation. The flow activation energy (Table 1) was found to be 105.1 kJ/mole for EMAAZn-59 and 95.9 kJ/mole for EMAANa-54. A comparison of the dynamic melt rheological properties of EMAA with its zinc ionomer and sodium ionomer shows that the melt viscosities (Table 2) and the flow activation energies are in the order EMAA < EMAANa-54 < EMAAZn-59.

Comparison of the Melt Flow Behavior of EAA-Based and EMAA-Based Ionomers

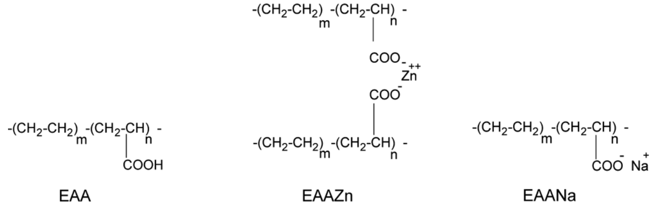
The EAAZn-63 shows lower flow activation energy (Table 1) as compared to EMAAZn-59. The flow activation energy of EAANa-58 was higher than that of EMAANa-54. Although the reason for the disparity in flow activation energies in the case of EAA series and the EMAA series ionomers is not fully understood, it appears that the ionic aggregation in the two series of ionomers are dissimilar. Ionic aggregation is the basis for the morphologies of ionomers. The ionic groups in ionomers are postulated to exist in two distinct environments, multiplets and clusters [14].

Multiplets are smaller aggregates of ion pairs distributed in the matrix. The ion pairs in the multiplets are believed to anchor the polymer chains at the point to which they are attached, thereby reducing the mobility of the chain in the immediate vicinity of the multiplets, with the mobility increasing gradually with increasing distance from the multiplet [15]. Thus the multiplets act as thermo-reversible (pseudo) ionic crosslinks and affect the properties of the matrix [16–17].

The greater flow activation energies suggest stronger ionic interactions [18] due to the presence of larger number of multiplets. The greater flow activation energies of sodium ionomer of the EAA series (EAANa-58), and the zinc ionomer of the EMAA series (EMAAZn-59) may be due to the presence of larger number of multiplets in these materials, which act as ionic crosslinks.

When sufficient numbers of multiplets are close enough together to form a contiguous region of restricted mobility, the region constitutes a much larger aggregate known as cluster. Clusters are envisioned to be of the order of 5 to 10 nm in diameter [19]. The number of ion pairs existing in clusters is believed to depend on factors such as the polarity of the polymer matrix, ionic functionality, and the temperature. As more and more clusters are formed the ionomeric material is correspondingly depleted of the number of thermo-reversible ionic crosslinks due to multiplets. This could result in a corresponding reduction in the flow activation energy. The lower flow activation energy of the zinc ionomer of the EAA series (EAAZn-63), and the sodium ionomer of the EMAA series (EMAANa-54) is presumably due to the formation of larger number of clusters in these materials. The chemical structures of the base materials and the ionomers used in the present investigations are shown in Scheme 1 and Scheme 2.

Table 2 shows the complex viscosities of the materials noted from the master curves at the angular frequencies of 10^{-1}, 10°, and 10^{1} (rad/s). The relaxation mode distribution of the base materials and the ionomers in the linear viscoelastic regime is evident from the

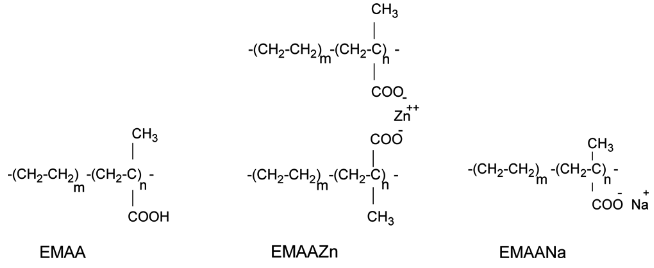


SCHEME 1 Chemical structure of poly(ethylene-*co*-acrylic acid), zinc salt of poly(ethylene-*co*-acrylic acid), and sodium salt of poly(ethylene-*co*-acrylic acid).

decrease in viscosity (η^*) with increasing angular frequency (ω). The viscosity of the unfunctionalized EAA was lower (about 72%) as compared to the viscosity of the unfunctionalized EMAA at all three frequencies. A comparison of the viscosity values of the ionomers at the three frequencies shows the order EAAZn-63 $<$ EMAAZn-59 and EAANa-58 $>$ EMAANa-54. The comparison of the viscosity values gives credence to the comparison of activation energy values, and indicates that the morphologies of the zinc and sodium ionomers of EAA are quite different as compared to the morphologies of the corresponding ionomers of EMAA [18].

All the ionomers show rapid decrease in viscosity as compared to the base EAA and EMAA as the angular frequency is increased from 10^{-1} to 10^{1} (rad/s) (Table 2). This could be attributed to a break down of the physical bonding of the polymer chains due to ionic crosslinks (multiplets), as the shear (angular frequency) increases [20]. The shear sensitivity of the ionomer is very useful in many polymer-processing applications.

EAA shows 43.5% reduction in viscosity as the angular frequency is increased from 10^{-1} to 10^{1} (rad/s). The corresponding reductions in the viscosity in the case of EAAZn-63 and EAANa-58 were 90.4% and 90.8%, respectively. EMAA shows 45% reduction in viscosity on



SCHEME 2 Chemical structure of poly(ethylene-*co*-methacrylic acid), zinc salt of poly(ethylene-*co*-methacrylic acid), and sodium salt of poly(ethylene-*co*-methacrylic acid).

increasing angular frequency from 10^{-1} to 10^{1} (rad/s). The corresponding reductions in the viscosity in the case of EMAAZn-59 and EMAANa-54 were 92.4% and 85.5%, respectively.

The viscosity reduction on increasing angular frequency was in the order EAAZn-63 $<$ EMAAZn-59, and EAANa-58 $>$ EMAANa-54. These observations are in tune with the observations in the case of flow activation energies. The larger reduction in viscosity in the case of the zinc ionomer of the EMAA series (EMAAZn-59), and the sodium ionomer of the EAA series (EAANa-58) indicates the presence of a larger number of shear sensitive pseudo crosslinks (multiplets) in these materials that are affected by the shear due to the increase in angular frequency (ω). The comparatively lower reduction in viscosity shown by the zinc ionomer of the EAA series (EAAZn-63), and the sodium ionomer of the EMAA series (EMAANa-58) may be due to the comparatively lesser number of crosslinks due to the multiplets that are affected by shear, as more ionic groups in these materials are assumed to be in the larger number of clusters present in these materials.

CONCLUSIONS

Dynamic melt rheological properties of EAA series and EMAA series ionomers and their base materials have been investigated. The difference in the linear viscoelastic spectra and flow activation energies of the two series of ionomers may be ascribed to the difference in the molecular structure. The time-temperature superposition rule was applicable for all the materials studied. The temperature dependence of the shift factors followed Arrhenius-type relation, enabling activation energies for viscous flow of the materials to be calculated. Although neutralization by zinc and sodium resulted in increase in the flow activation energy of EAA, the effect was more pronounced in the case of the sodium ionomer. In the case of EMAA based ionomers, neutralization by zinc caused larger increase in the flow activation energy, as compared to the neutralization by sodium. Incorporation of ionic groups results in raising the melt viscosity by several orders of magnitude in the case of ionomers as compared to the parent unfunctionalised EAA and EMAA. The ionomers are more shear sensitive, as compared to the base materials.

REFERENCES

[1] Agarwal, P. K., Makowski, H. S., and Lundberg, R. D., *Macromolecules* **13**, 1679 (1980).
[2] Ding, J., Xue, G., Yang, C., and Chen, R., *J. Appl. Polym. Sci.* **45**, 1087 (1992).

[3] Peiffer, D. G., Hager, B. L., Weiss, R. A., Agarwal, P. K., and Lundberg, R. D., *J. Polym. Sci. Polym. Phys. Edn.* **23**, 1869 (1985).

[4] Dasgupta, A. M., David, D. J., and Misra, A., *J. Appl. Polym. Sci.* **44**, 1213 (1992).

[5] Vanhoorne, P. and Registter, R. A., *Macromolecules* **29**, 598 (1996).

[6] MacKnight, W. J. and Lundberg, R. D., *Rubb. Chem. Technol*. **57**, 652 (1984).

[7] Fan, X. D. and Bazuin, C. G., *Macromolecules* **26**, 2508 (1993).

[8] Takahashi, T., Watanabe, J., Minagawa, K., and Koyama, K., *Polymer* **35**, 5722 (1994).

[9] Stier, U., Schawaller, D., and Oppermann, W., *Polymer* **42**, 8753 (2001).

[10] Vega, J. F., Santamaria, A., Munoz-Escalona, A., and Lafuente, P., *Macromolecules* **31**, 3639 (1998).

[11] Malmberg, A., Kokko, E., Lehmus, P., Lofgren, B., and Seppala, J. V., *Macromolecules* **31**, 8448 (1998).

[12] Zhang, H., Li, S., and Luo, H., *J. Appl. Polym. Sci.* **34**, 1353 (1987).

[13] Xie, H. Q., Ao, Z. P., and Guo, J. S., *J. Macromol. Sci. Phys*. **B34**, 249 (1995).

[14] Visser, S. A. and Cooper, S. L., *Macromolecules* **24**, 2584 (1990).

[15] Eisenberg, A., Hird, B., and Moore, R. B., *Macromolecules* **23**, 4098 (1990).

[16] Fujimura, M., Hashimoto, T., and Kawai, H., *Macromolecules* **15**, 136 (1982).

[17] Eisenberg, A. and Kim, J. S. (1998). *Introduction to Ionomers*, Wiley- Interscience, p. 47ff.

[18] Hsieh, T. T., Tiu, C., and Simon, G. P., *Polymer* **42**, 1931 (2001).

[19] Takei, M., Tsujita, Y., Shimada, S., Ichihara, H., Enokida, M., Takizawa, A., and Kinoshito, T., *J. Polym. Sci., Polym Phys. (Ed.)* **26**, 997 (1988).

[20] Hendy, B. N. (1998). In *Specialty Polymers*. R. W. Dyson, Ed., Blackie Academic & Professional, p. 136ff.