

The effects of local glass transition temperatures of ionic core–shell structures on the tensile behavior of sodium-neutralized poly(ethylene-co-methacrylic acid) ionomer/lauric acid blends

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ABSTRACT

Local glass transition temperatures (T_g) for ionic aggregates, in sodium-neutralized poly (ethylene-co-methacrylic acid) (EMAA) ionomers plasticized with lauric acid (LA), have been position-selectively measured by electron spin resonance (ESR). This ESR study reveals that a restricted shell region surrounds the rigid ionic core with a thickness of approximately 10 Å. Here, we directly observed that the shell region is preferentially plasticized by LA. When the local shell region T_g decreases to below room temperature, while the weight fraction of LA simultaneously increases, the specimen becomes remarkably stretchable during the tensile test. Based on these results, we suggest that ionic core–shell structures, which have rubbery shells, act as a sort of loose physical cross-link, under stretching behavior, due to the tendency of some carboxylic and/or carboxylate groups, attached to highly stressed polyethylene chains, to detach from the ionic cores.

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1. Introduction

Polymers that contain small amounts of ionic groups, which are covalently bound to the main hydrophobic chain, are called ionomers [1–6]. Poly (ethylene-co-methacrylic acid) (EMAA) ionomers, in which carboxylic groups are partially neutralized by metal ions, such as Na^+ and Zn^{2+} , are important in industrial material applications and are widely used in packaging, coatings, and bonds because of their superior impact resistance, elasticity, melt strength, and adhesiveness [7,8].

Ionic groups aggregate within the hydrophobic polymer matrix and form small spherical ionic cores with diameters of 1–2 nm. The ionic core is an aggregate that consists of several ion pairs, known as “ionic multiplet” [6,9]. Eisenberg et al. reported that the ionic core is surrounded by a “shell” consisting of polymer segments that have restricted mobility [6,9]. The ionic core size is known to be insensitive to the ion content of the ionomer because the ionic group aggregation is limited by steric interactions between polymer chains that surround the ionic core. As the ion content increases, the average distance between the ion cores decreases. Consequently, some overlap occurs among restricted shell

regions. Increasing overlap forms a relatively large contiguous region of restricted mobility. This contiguous region is known as the “ionic cluster” [6,9].

Selective plasticization of ionic clusters and hydrophobic matrix regions within ionomers is an important control on the melt viscosity for industrial processes and solid mechanical properties in material applications [10–17]. In general, nonpolar plasticizers (e.g., dioctyl phthalate) selectively plasticize the hydrophobic matrix regions of ionomers, whereas polar plasticizers (e.g., glycerol) selectively plasticize ionic cluster regions. Moreover, surfactants (e.g., sodium dodecylbenzenesulfonate) preferentially and slightly plasticize ionic clusters and matrix regions in ionomers, respectively [13,14]. The effects of plasticization on ionomers have, to date, generally been examined by dynamic mechanical analysis (DMA) measurements [10,11,13,14,16,17].

Recently, the authors developed a method, via electron spin resonance (ESR) with a position-selective spin-probing technique, that selectively and precisely measures the local glass transition temperature (T_g) gradient that surrounds ionic cores contained in EMAA ionomers [18]. This technique position-selectively determines the local ionic core and shell region T_g values within the EMAA ionomer, neutralized with sodium. Based on this measurement technique, we reported that the EMAA ionomer ionic core is glassy (local $T_g = 320$ K) at room temperature, and the restricted

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shell region's thickness is approximately 1.0 nm. We also found that the local shell region T_g gradually decreases with separation from the ionic core.

In this study, we applied the ESR technique to directly and quantitatively monitor the plasticization effect that lauric acid (LA) has on and around the ionic core within the EMAA ionomers. This ESR study suggests that LA preferentially decreases the local restricted shell region T_g because the LA's carboxylic group becomes part of the ionic core, and the LA's flexible tail locates in the shell region. When 10 wt.% LA is mixed with the EMAA ionomer, the restricted shell surrounding the glassy ionic core becomes rubbery at room temperature. This specimen exhibited remarkably soft and stretchable properties compared with the virgin EMAA ionomer during the tensile test. In the present study, we examined the relationships between the rigidity of the ionic core–shell structure and the mechanical behavior of the EMAA ionomers.

2. Methods

2.1. Sample preparation

2.1.1. Materials

EMAA ionomers were provided by the Technical Center, Du Pont-Mitsui Polychemicals Co. Ltd., Chiba, Japan. The EMAA ionomer contains 5.4 mol% methacrylic acid units in the backbone and 54% of the COOH group is neutralized with sodium. We define the notation of this ionomer as EMAA54Na. Low-density polyethylene (LDPE) is MIRASON from Mitsi Chemicals Co., Ltd., Chiba, Japan. LA (>98%) was purchased from Kishida Chemical Co., Ltd. The EMAA ionomer and LA chemical structures are shown in Fig. 1(A) and (B), respectively. Acetone (extra pure reagent) was purchased from Nacalai Tesque Inc. and used without further purification. 5-DOXYL-stearic acid (5DSA), 7-DOXYL-stearic acid (7DSA), 10-DOXYL-stearic acid (10DSA), and 10-DOXYL-nonadecane (10DND) were obtained from Aldrich Chemical Co., Ltd. 12-DOXYL-stearic acid (12DSA) was purchased

from Santa Cruz Biotechnology. The first four spin probes (i.e., 5DSA, 7DSA, 10DSA, and 12DSA) have structures based on stearic acid, and the fifth spin probe (i.e., 10DND) has a nonadecane structure. The chemical structures of the spin probes are shown in Fig. 1(C). The spin probes differ with respect to their polarity and/or position in the nitroxide group with respect to the headgroup; the number in each spin-probe label represents the nitroxide group position.

2.1.2. Preparation of Blend Samples

Blend samples that consist of EMAA54Na and LA were prepared using a DSM miniextruder using a twin screw configuration at 453 K. EMAA54Na/5 LA and EMAA54Na/10 LA contain 5 and 10 wt.% LA, respectively. The degree of total neutralization, for EMAA54Na/10 LA, is 41%. Therefore, we prepared EMAA41Na, which also has a degree of total neutralization of 41%, by a melt blend of the EMAA54Na and EMAA at 453 K. The ionomer samples that were used in this study were press-molded at 423 K into sheets with a thickness of 0.5 mm. These press-molded sheets, sandwiched between two stainless steel plates, were quenched using packed ice water.

2.1.3. Spin-Probing

Ionomer sheets were cut into small pieces (ca. 10 mm × 2 mm × 0.5 mm) and immersed in distilled water at room temperature for one week. Spin probes were dissolved in a small amount of acetone and then added to distilled water to form an aqueous solution of 0.1 mM. Ionomer pieces were immersed in the aqueous probe solution for four days. The ionomer pieces were dried under vacuum at room temperature for 12 h and additionally dried at 353 K for 48 h. The dried ionomers were quickly encapsulated into 5 mm o. d. quartz tubes for ESR measurements and sealed under vacuum, followed by further drying under vacuum at room temperature and 393 K for 12 h and 10 min, respectively. Ionomer spin-probe concentrations were adjusted to sufficiently low levels to avoid line broadening caused by spin–spin interactions.

2.2. Measurements

2.2.1. ESR

We analyzed ESR spectra with a JEOL X-band (ca. 9 GHz) FA100 spectrometer with a 100 kHz field modulation. The modulation amplitude, magnetic field width, sweep time, time constant, and number of scans were typically 0.25 mT, 15 mT, 20 s, 0.01 s, and 3, respectively. The magnetic field and g tensor were calibrated with Mn^{2+} . Microwave power used for measurements with and without microwave power saturation (MPS) was 16 and 0.02 mW, respectively. Before measurements, the sample was heated at 373 K for 10 min and then quenched at 203 K in the ESR cavity; measurements were performed from 223 to 373 K, with intervals of 2.5 K. In these experiments, we used an automatic measurement program. The tuning parameters (phase and detector current) of the ESR spectrometer and the sample position in the cavity were kept constant, and the temperature was varied only for MPS measurements. MPS measurement principles are described in detail elsewhere [19–21].

2.2.2. Differential Scanning Calorimetry (DSC)

DSC measurements, calibrated with indium, zinc, lead, and tin standards, were performed using a DSC7020 differential scanning calorimeter manufactured by SII. The DSC cell was purged with dry nitrogen gas during the measurement with a flow rate of 40 mL min⁻¹. Prior to DSC measurements, a sample piece, sealed in an aluminum pan, was heated at 423 K for 10 min and quenched to

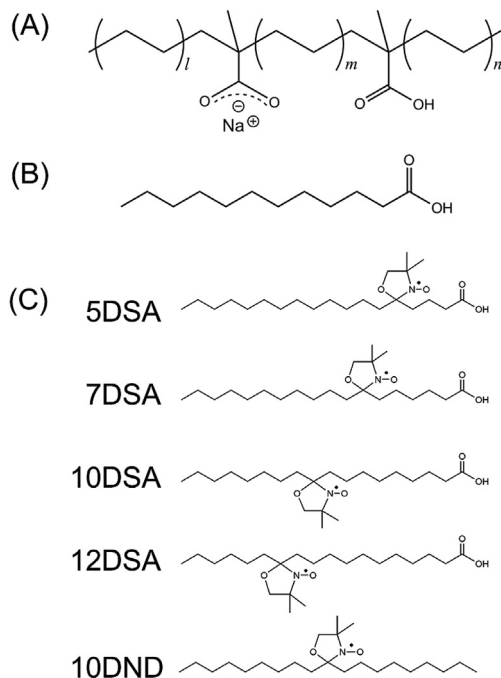


Fig. 1. Chemical structures of (A) the EMAA ionomer, (B) the LA, and (C) the spin probe.

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