Preparation and Li^+ Conductivity of Highly Deproteinized Natural Rubber Having Epoxy Group

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Abstract

Highly deproteinized natural rubber having epoxy group (LENR) was applied to transport Li^+ as an ionic conducting medium. LENR was prepared by epoxidation of deproteinized natural rubber followed by oxidative degradation with $(NH_4)_2S_2O_8$ and propanal. The resulting liquid rubber ($M_n \approx 10^4$) was found to have well defined terminal groups, i.e. aldehyde group and α-β unsaturated carbonyl group, which is useful for further chemical modification, without loss of epoxy group. The glass transition temperature (T_g) and gel content of natural rubber increased after epoxidation whereas they decreased after degradation. LENR was confirmed to have a potential application as an ionic conducting medium due to high polarity and mobility, necessary for a solid polymer electrolyte.

1. Introduction

Solid polymer electrolyte has been widely recognized to be an important material to fabricate polymer battery, because it provides an ionic conducting medium through which Li^+ transports effectively[1, 2]. For the polymer, it has been essential to achieve low glass transition temperature, T_g, and low melting temperature, T_m, even though it contains polar substituents that result in higher T_g and T_m. In this respect, oligomer electrolytes were prepared to reduce T_g and T_m. However, the resulting oligomer was physically unstable; for instance, it tended to spread out. To overcome such an antinomy, we pay attention to rubbery polymers having low T_g and T_m.

Natural rubber, isolated from *Hevea brasiliensis*, consists mainly of *cis*-1,4-isoprene unit which can be chemically modified with peracetic acid or performic acid to introduce polar epoxy group into the rubber[3, 4, 5]. In the previous works [5, 6, 7], the epoxidation of natural rubber with excess amount of formic acid and hydrogen peroxide was reported to produce mostly ring-expanded and ring-opened secondary derivatives that formed three-dimensional networks. Furthermore, T_g of the epoxidized natural rubber rose from 204 K to 264 K, corresponding to the increase in the epoxy group content from 0 to 75 mol-%[4]. The ionic conductivity of commercial epoxidized natural rubber containing about 50 mol-% epoxy group was relatively low, compared to polyether[8]. Thus, it is of interest to prepare liquid epoxidized natural rubber having well-defined terminal groups which are useful for chemical modification,

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crosslinking and so forth, for the sake of the application to polymer battery, as the solid polymer electrolyte.

In the present work, natural rubber, which was purified by deproteinization with proteolytic enzyme and surfactant (DPNR), was epoxidized in the latex state with freshly prepared peracetic acid followed by degradation with peroxide in the presence of propanal. The change in T_g of the ENR and epoxidized DPNR (EDPNR) was investigated in relation to the epoxy group content and molecular weight. The resulting liquid EDPNR was applied to transport Li^+.

2. Experimental

Rubber samples used in this study were fresh natural rubber latex. Deproteinization of the rubber was made by incubation of the latex with 0.04 wt % enzyme (KP-3939) and 1.0 wt % sodium dodecyl sulfate (SDS) for 12 hrs at 305 K followed by centrifugation[10]. The cream fraction was redispersed into 1.0 wt % SDS solution and washed twice by centrifugation.

Natural rubber (NR) and deproteinized natural rubber (DPNR), pre-cooled at 283 K, were epoxidized in the latex state with fresh peracetic acid (33 v/v % concentration) for 3 hrs at pH 5-6. After completion of the reaction, pH of the solution was adjusted to 7.1 and a part of the rubber was coagulated by adding an excess of methanol. The rubber was soaked in water for a day and dried under reduced pressure at 303 K for a week[11].

The degradation of the epoxidized rubber was carried out by incubation of the latex with ammonium persulfate ($(NH_4)_2S_2O_8$) and propanal at 333 K for 12 hrs[9]. The resulting latex was coagulated with methanol followed by purification with toluene and methanol, and dried up at 303 K for a week under reduced pressure. The procedure to prepare the samples was schematically represented in Figure 1.

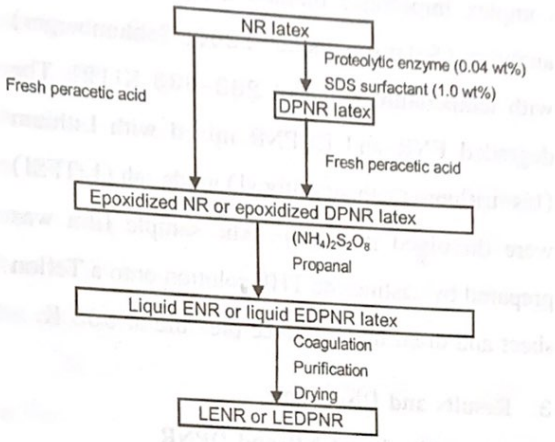

Fig. 1 *– Schematic illustration of preparing ENR, EDPNR, degraded ENR and degraded EDPNR.*

Measurements of molecular weight and molecular weight distribution of the rubbers were made by a TOSOH size exclusion chromatography (SEC), consisting of a TOSOH CCPD pump, RI-8012 Differential Refractometer and UV-8011 UV detector. The flow rate of the mobile phase, THF, was 0.5 ml/min.

The gel content was determined by swelling the rubber into dried toluene under the dark for a week. The gel fraction was separated by centrifugation at 11,000 g for 30 min.

^{1}H-NMR measurement was carried out by a JEOL EX-400 NMR spectrometer at the pulse repetition time of 7 sec for 45° pulse.

DSC measurement was made with a Seiko Instruments DSC 220 differential scanning calorimeter over the temperature range of 153 K to 373 K at the heating rate of 10 K/min.

The ionic conductivity was measured by the complex impedance method using an impedance analyzer (Solartron model 1260; Schlumberger) with temperature range of 283-333 K[12]. The degraded ENR and EDPNR mixed with Lithium (bis-trifluoro methanesulfonyl) imide salt (LiTFSI) were dissolved into THF. The sample film was prepared by casting the THF solution onto a Teflon sheet and dried under reduce pressure at 303 K.

3. Results and Discussion

3.1 Epoxidiation of NR and DPNR

Figure 2 shows signals characteristic of methyl, methylene and unsaturated methylene protons of isoprene units for NR, DPNR, epoxidized NR (ENR) and epoxidized DPNR (EDPNR) appeared at 1.6, 2.1 and 5.1 ppm, respectively. After epoxidation of NR and DPNR, other two signals appeared at 2.7 and 1.2 ppm, which were assigned to methine and methyl protons of the resulting epoxy group, respectively. The epoxy group content was significantly dependent upon the feed of peracetic acid: the content of ENR being similar to that of EDPNR when the feed of peracetic acid was the same. This is consistent with the result reported in the previous paper[11], suggesting little effect of proteins present in natural rubber on the epoxidation.

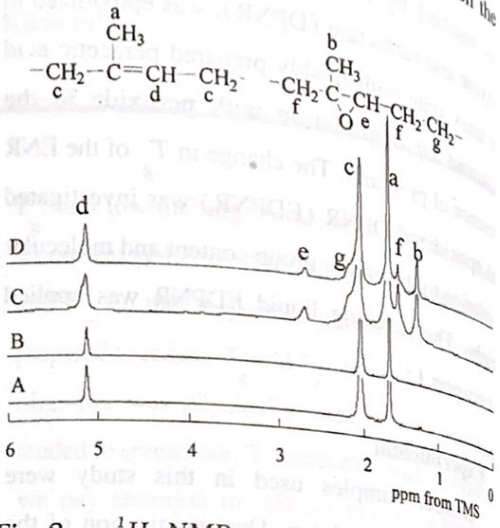

Fig. 2 ^{1}H-NMR spectra of (A) NR, (B DPNR, (C) ENR2 and (D) EDPNR2.

Table 1 shows gel content (C_{gel}), T_g an epoxy group content (X_{epoxy}) for the epoxidize rubbers. The higher the epoxy group content th higher was gel content and T_g. The increase in g content may be attributed to any side reactior that occurred during epoxidation[13, 14], as we as a ring-opening of epoxy groups, to form a thr dimensional network structure[1,5,15].

Table 1 Characteristics of ENR, DPNR, LENR and LEDPNR

Specimens	$M_n/10^5$	M_w/M_n	X_{epoxy} / mol %	T_g / K	C_{gel} / wt %
NR	3.37	7.45	-	212	8.9
LENR1	0.46	3.84	11 (9.6)*	222 (221)*	0 (12)
LENR2	0.38	3.19	29 (28)	238 (235)	0 (48)
LENR3	0.23	4.53	43 (38)	250 (245)	0 (61)
DPNR	2.10	8.48	-	213	1
LEDPNR1	0.53	3.58	4.4 (3.9)	217 (217)	0 (27)
LEDPNR2	0.46	3.51	19 (16)	228 (228)	0 (64)
LEDPNR3	0.31	4.45	39 (33)	245 (244)	0 (77)

* The values in parentheses are the data for the epoxidized natural rubber.

The formation of network structure is known to raise T_g due to a suppression of micro-Brownian movement[16]. This suggests that the change in T_g for ENR and EDPNR is associated with not only increase in epoxy group content but also gel content. Thus, to reduce T_g, even at high epoxy group content, it is necessary to degrade molecular weight of ENR and EDPNR.

3.2 Epoxidation and Degradation of NR and DPNR

After degradation, ENR and EDPNR were thoroughly soluble in toluene, THF and chloroform, so that the rubbers were subjected to SEC measurement. Figure 3 shows typical SEC curves for the degraded EDPNR (EDPNR-deg), in which distribution is unimodal and symmetrical. From the curve, average molecular weights of degraded ENR (ENR-deg) and EDPNR-deg were estimated, on the basis of the molecular weight of standard polystyrene. The estimated values of number average molecular weight, and M_w/M_n are tabulated in Table 1.

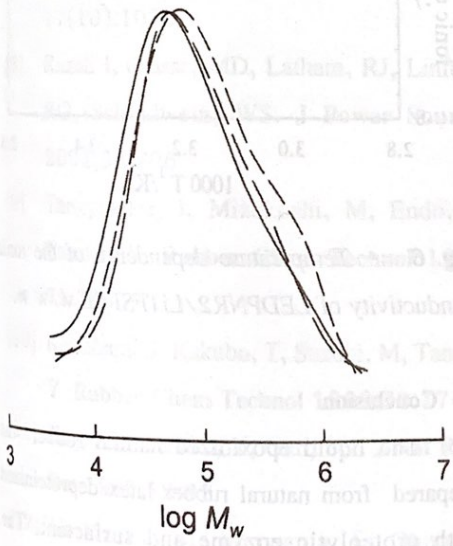

Fig.3 - GPC curves of LEDPNR; LEDPNR1 (_ _), LEDPNR2 (____) and LEDPNR3 (_ _ _).

The M_n decreased significantly after degradation, and the molecular weight distribution was narrowed, as indicated by the M_w / M_n values. These are consistent with the previous results obtained for NR and DPNR after degradation[9]. Since we adopted the oxidative degradation with peroxide to epoxidize the rubbers, as well as NR and DPNR, most of the chain scission reactions should occur at the double bond of isoprene units, in accordance with the manner proposed in the previous paper[9]. This implies that the liquid rubber from EDPNR may have well-defined terminal units, but one from ENR may not.

^{1}H-NMR spectrum of LEDPNR2 is shown in Figure 4. Two signals appeared at 9.4 and 9.8 ppm after degradation, except for isoprene units and epoxy group, without any other signals. These were assigned to aldehydric protons of the α-β unsaturated aldehyde and aldehyde attached to a methylene group of the terminal units, respectively. This is a strong evidence showing that LEDPNR2 is a liquid rubber having well-defined terminal units, as in the case of LDPNR[9]. However, these signals were not clearly found in the spectrum of LENR. This may be due in part to the presence of non-rubber components that produce by-products through side reactions. Furthermore, after degradation, an increase in epoxy group content of ENR and EDPNR was also confirmed, as shown in the ^{1}H-NMR spectrum. The estimated increase in epoxy group content is shown in Table 1, being less than 5%, which is attributed to a side reaction of peroxide used in the present study. The resulting rubber is, thus, confirmed to be a telechelic liquid EDPNR, having aldehyde, ketone and α-β unsaturated carbonyl groups at the terminal of the rubber chain, without any loss of epoxy group.

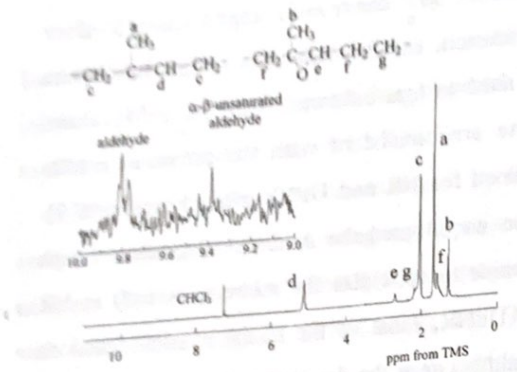

Fig. 4 - ^{1}H-NMR spectra of LEDPNR2.

The decrease in molecular weight and increase in epoxy group content resulted in a change in T_g for ENR and EDPNR, as shown in Table 1. Even though there were significant changes in molecular weight and epoxy group content, T_g increased within several degrees, raging from 0 to 5K. This may be because the active micro-Brownian movement due to the reduction of molecular weight suppressed the increase in T_g with increasing epoxy group content.

The resulting liquid EDPNR was applied to a medium to transport Li^+ as a solid polymer electrolyte to fabricate Li-polymer battery. A typical Cole-Cole plot for a mixture of LEDPNR2 with LiTFSI salt is shown in Figure 5.

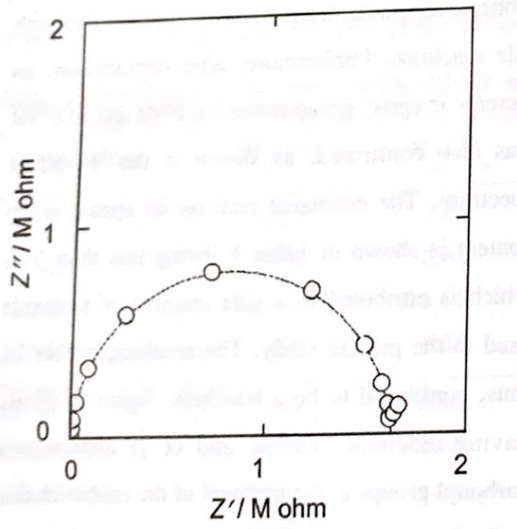

Fig. 5 - Cole-Cole plot of LEDPNR2/LiTFSI 20 w/w % at 323K.

The imaginary part of impedance, Z", was dependent upon the real part, Z', to form half circle. Thus, the bulk resistance (R_b) was determined to be a point of intersection of the curve and axis of abscissa[17]. An ionic conductivity, estimated from R_b, is shown in Figure 6, as a function of reciprocal temperature. The ionic conductivity of LEDPNR2 mixed with 20w/w% LiTFSI increased as the temperature rose. The ionic conductivity was about 3.8×10^{-5} S cm^{-1} at 332 K, corresponding to that of polyether[18-19]. This demonstrates the possibility of liquid EDPNR as a solid polymer electrolyte due to high polarity and mobility, necessary for the solid polymer electrolyte.

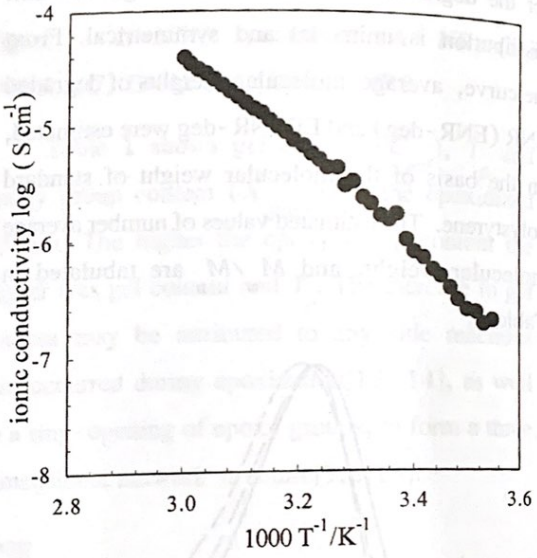

Fig. 6 - Temperature dependence of the ionic conductivity of LEDPNR2/LiTFSI 20 w/w %.

4. Conclusion

The liquid epoxidized natural rubber was prepared from natural rubber latex deproteinized with proteolytic enzyme and surfactant. The resulting liquid rubber showed low T_g, low M_n, and well-defined terminal groups, i.e. aldehyde and

α-β unsaturated carbonyl groups. The ion-conductivity of the rubbers was 3.84×10^{-5} S/cm at 323 K, reflecting its high polarity and mobility.

5. Acknowledgement

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