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Depolymerization and ionic conductivity of enzymatically deproteinized natural rubber having epoxy group

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Abstract

Preparation of liquid epoxidized natural rubber (ENR) was made by oxidative depolymerization of ENR in latex stage without loss of epoxy group. Epoxidation of fresh natural rubber latex, which was purified by deproteinization with proteolytic enzyme and surfactant, was carried out with freshly prepared peracetic acid. The glass transition temperature (T_g) and gel content of the rubbers increased after the epoxidation, both of which were dependent upon an amount of peracetic acid. The gel content was significantly reduced by oxidative depolymerization of the rubber with $(NH_4)_2S_2O_8$ in the presence of propanal. The resulting liquid epoxidized rubber ($M_n \approx 10^4$) was found to have well-defined terminal groups, i.e. aldehyde groups and α-β unsaturated carbonyl groups. The novel rubber was applied to transport Li^+ as an ionic conducting medium, that is, solid polymer electrolyte.

Keywords: Liquid epoxidized natural rubber; Enzymatic deproteinization of natural rubber; Depolymerization; Ionic conductivity

1. Introduction

Epoxidation of natural rubber is a long-standing technique to improve the properties of the rubber such as solvent resistance [1], gas permeability [2] and mechanical properties [3], in addition to high tensile strength and tear strength that the rubber inherently holds. The epoxidation has been mainly carried out in latex stage using freshly prepared peracetic acid, performic acid, or the mixture of hydrogen peroxide and organic acid, i.e. formic acid or acetic acid. In the previous works, the epoxy groups of the rubber were confirmed to be stable under well-controlled condition [3,4]. In contrast, they resulted in mostly ring-expanded and ring-opened secondary derivatives in the presence of excess amounts of formic acid and hydrogen peroxide [5]. Thus, it is of interest to investigate the relationship between structure and properties of epoxidized natural rubber (ENR), especially in views of the epoxy group contents, distribution of epoxy groups, ring-opened or ring-expanded groups and so forth.

In the previous work [4], glass transition temperature (T_g) of the rubber was found to be dependent upon the epoxy group content; i.e. T_g rose from 204 to 264 K, corresponding to epoxy group content ranging from 0 to 75 mol%. However, three-dimensional networks were practically formed under strong acidic condition, as the epoxy group content increased. This makes us recognize

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the importance to depolymerize the rubber after the epoxdiation, in order to increase epoxy group content while decrease molecular weight.

In the previous work [6], we reported that the molecular weight of natural rubber was reduced by depolymerization of the rubber with peroxide in the presence of propanal in latex stage. Terminal groups of the products whose weight average molecular weight was about 1.8×10^4 were found to be aldehyde, ketone and α-β unsaturated carbonyl groups, when the rubber was purified with proteolytic enzyme and surfactant to prepare deproteinized natural rubber (DPNR) [6]. Thus, the epoxidation of DPNR followed by depolymerization may allow us to prepare telechelic epoxidized oligomer.

The low molecular weight ENR may have a potential to prepare a solid polymer electrolyte (SPE), because of its low T_g, high mobility of main chain molecule and high polarity to transport Li^+ as a medium. In fact, the ionic conductivity of masticated ENR50 was relatively low, compared to polyether [7]. In the present work, natural rubber, purified by deproteinization with proteolytic enzyme and surfactant, was epoxidized in the latex stage with freshly prepared peracetic acid followed by depolymerization with peroxide and 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^+, as a SPE.

2. Experimental

Rubber sample used in this study was fresh natural rubber latex, which was collected at a plantation of Malaysian Rubber Board just before deproteinization, epoxidation and depolymerization. Deproteinization of the rubber was made by incubation of the latex with 0.04 w/w% proteolytic enzyme (KaO, KP-3939) and 1.0 w/w% sodium dodecyl sulfate (SDS) for 12 h at 305 K followed by centrifugation [8]. The cream fraction was redispersed into 1.0 w/w% SDS solution and washed twice by centrifugation. Nitrogen content (N-content), gel content, weight average molecular weight, M_w, number average molecular weight, M_n, and M_w/M_n for natural rubber (NR) and DPNR were tabulated in Table 1.

NR and DPNR, pre-cooled at 283 K, were epoxidized in the latex stage with fresh peracetic acid (33 v/v% concentration) for 3 h 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 [9].

The depolymerization of the epoxidized rubber was carried out by incubation of the latex with ammonium persulfate ($(NH_4)_2S_2O_8$) and propanal at 338 K for 12 h. 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 Fig. 1.

Measurements of molecular weight and molecular weight distribution of the rubbers were made by a TOSOH size exclusion chromatograph (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 in dried toluene in the dark for a week. The gel fraction was separated by centrifugation at 11,000*g* for 30 min. The content of gel fraction, C_{gel}, was, estimated as follows:

$$C_{gel} = \frac{W_{gel}}{W_{rubber}} \times 100$$

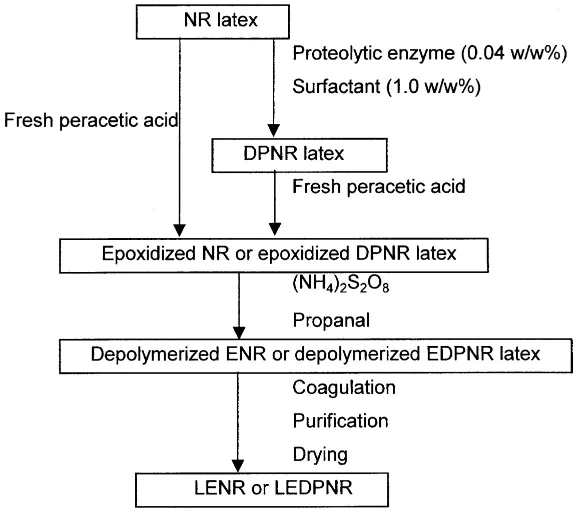

Fig. 1. Schematic illustration of preparing ENR, EDPNR, DENR and DEDPNR.

Table 1
Molecular characteristics of NR and DPNR

Specimen	N-content/w/w%	C_{gel}/w/w%	$M_w/10^5$	$M_n/10^5$	M_w/M_n
NR	0.340	8.9	3.37	25.1	7.45
DPNR	0.017	1.0	2.1	17.8	8.48

where W_{gel} and W_{rubber} are the weight of gel fraction and rubber, respectively.

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

DSC measurement was made with a Seiko Instruments DSC 220 differential scanning calorimeter over the temperature range of 153–373 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 [10]. The liquid epoxidized DPNR mixed with lithium bis(trifluoromethansulfonyl)imide salt (LiTFSI) were dissolved into THF. The sample film was prepared by casting the THF solution onto a Teflon sheet and dried under reduced pressure at 303 K.

3. Results and discussion

3.1. Epoxidation of NR and DPNR

A typical ^{1}H-NMR spectrum for NR, DPNR, ENR and EDPNR is shown in Fig. 2. Signals characteristic of methyl, methine and unsaturated methylene protons of isoprene units 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, X_{epoxy}, was, thus, estimated from intensity ratio of the signals, as follows:

$$X_{epoxy} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100$$

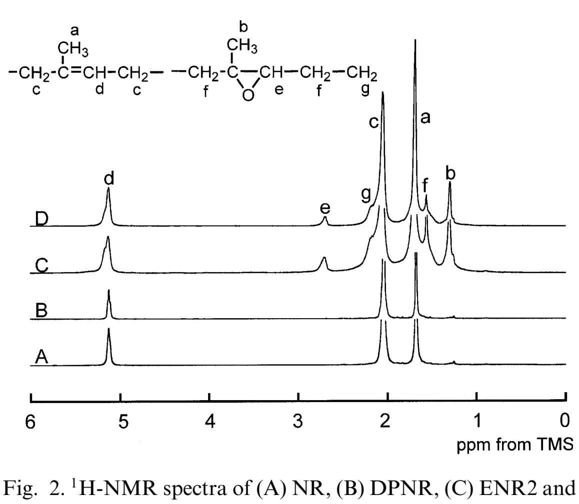

Fig. 2. ^{1}H-NMR spectra of (A) NR, (B) DPNR, (C) ENR2 and (D) EDPNR2.

Table 2
Epoxy group content, glass transition temperature and gel content of ENR and EDPNR

Specimen	X_{epoxy}/mol%	T_g/K	C_{gel}/w/w%
NR	–	212	8.9
ENR1	9.6	221	12
ENR2	28	235	48
ENR3	38	245	61
DPNR	–	213	1
EDPNR1	3.9	217	27
EDPNR2	16	228	64
EDPNR3	29	239	63
EDPNR4	33	244	77

where I is intensity of the signals and the subscript represents chemical shift. The estimated epoxy group content of the rubber was tabulated in Table 2. The epoxy group content was significantly dependent upon an amount of peracetic acid: the content of ENR being similar to that of EDPNR when the amount 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. 3 shows gel content and T_g versus epoxy group content for the epoxidized rubbers. The higher the epoxy group content the higher was gel content and T_g. The increase in gel content may be attributed to any side reactions that occurred during epoxidation [11], as well as a ring-opening of epoxy groups, to form a three dimensional network structure [1,5,12]. The formation of network structure is known to rise T_g due to a suppression of micro-Brownian movement [13]. 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 depolymerize the molecular weight of ENR and EDPNR.

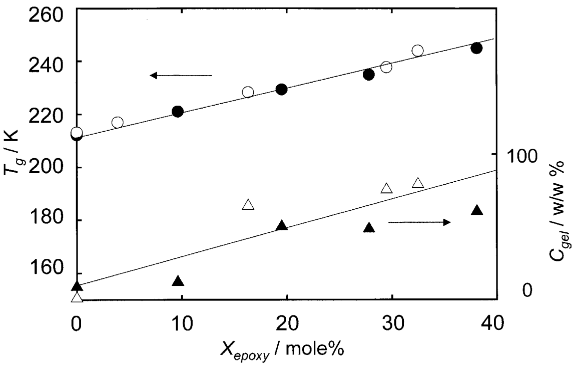

Fig. 3. Glass transition temperature of ENR (●) and EDPNR (○) and gel content of ENR (▲) and EDPNR (△) versus epoxy group content.

3.2. Epoxidation and depolymerization of NR and DPNR

After depolymerization, ENR and EDPNR were thoroughly soluble in toluene, THF and chloroform, so that the rubbers were subjected to SEC measurement. Fig. 4 shows typical SEC curves for the depolymerized EDPNR (DEDPNR), in which the distribution is unimodal and symmetrical. From the curve, average molecular weights of depolymerized ENR (DENR) and DEDPNR were estimated, on the basis of the molecular weight of standard polystyrene. The estimated values of number average molecular weight, M_n, weight average molecular weight, M_w, and M_w/M_n are tabulated in Table 3. The M_n and M_w decreased significantly after depolymerization, and the molecular weight distribution was narrowed, as is evident from M_w/M_n. These are consistent with the previous results obtained for NR and DPNR after depolymerization [6]. Since we adopted the oxidative depolymerization with peroxide for the epoxidized rubbers, as well as NR and DPNR, most chain scission should occur at the double bond of isoprene units, in accordance with the manner proposed in the previous paper [6].

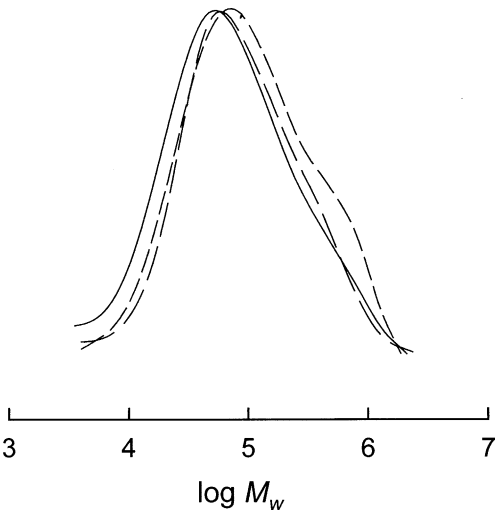

Fig. 4. GPC curves of depolymerized EDPNR; DEDPNR1 (- - -), DEDPNR2 (– – –) and DEDPNR4 (—).

^{1}H-NMR spectrum of DENR2 and DEDPNR2 are shown in Fig. 5. Two signals appeared at 9.4 and 9.8 ppm after depolymerization for EDPNR2, 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 that DEDPNR2 is a liquid rubber having well-defined terminal units, as in the case of depolymerized DPNR. However, these signals were not clearly shown for DENR. This may be due in part to the presence of non-rubber components that may produce by-products through any side reactions. Furthermore, after depolymerization, the increase in epoxy group content was also confirmed for the ENR and EDPNR, as shown in the ^{1}H-NMR spectrum. The estimated increase in epoxy group content is shown in Table 3, being less than 5%, which is attributed to a side reaction of peroxide used in the present study. The resulting DEDPNR 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 loss of epoxy groups, as in the case of Tangpakdee et al.

The decrease in molecular weight and increase in epoxy group content resulted in a change in T_g for DENR and DEDPNR, as shown in Table 3. Even after the significant change in molecular weight and epoxy group content, T_g increased within several degrees, raging from 0 to 5 K. This may be due to the reduction of molecular weight.

The resulting DEDPNR was applied to a medium to transport Li$^+$ as a SPE to fabricate a Li-polymer battery. A typical Cole–Cole plot for a mixture of DEDPNR3 with LiTFSI is shown in Fig. 6. The imaginary

Table 3
Characteristics of DENR and DEDPNR

Specimen	$M_n/10^5$	$M_w/10^5$	M_w/M_n	X_{epoxy}/mol%	T_g/K	C_{gel}/w/w%
NR	3.37	25.1	7.45	–	212	8.9
DENR1	0.46	1.76	3.84	11 (9.6)[a]	222 (221)[a]	0
DENR2	0.38	1.21	3.19	29 (28)	238 (235)	0
DENR3	0.23	1.04	4.53	43 (38)	250 (245)	0
DPNR	2.10	17.8	8.48	–	213	1.0
DEDPNR1	0.53	1.89	3.58	4.4 (3.9)	217 (217)	0
DEDPNR2	0.46	1.61	3.51	19 (16)	228 (228)	0
DEDPNR3	0.18	0.41	2.29	33 (29)	243 (239)	0
DEDPNR4	0.31	1.38	4.45	39 (33)	245 (244)	0

DENR: depolymerized ENR; DEDPNR: depolymerized EDPNR.

[a] The values in parentheses are the data for the ENR.

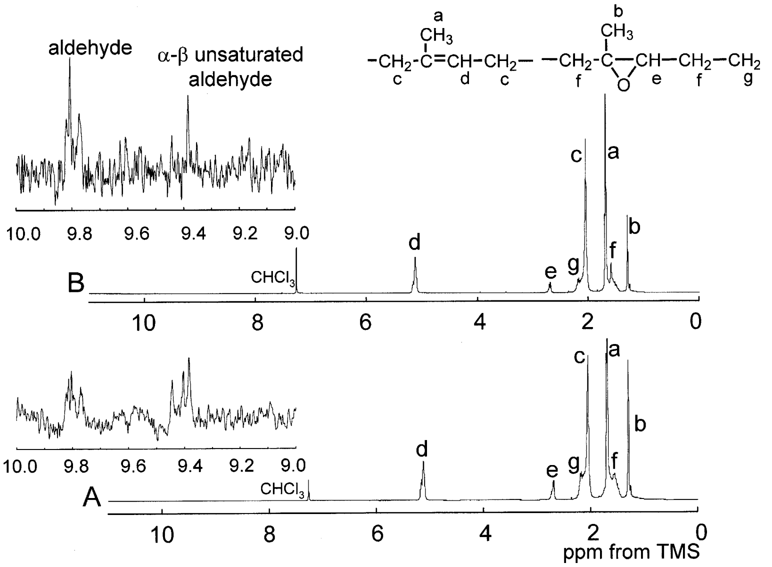

Fig. 5. ^{1}H-NMR spectrum of (A) DENR2 and (B) DEDPNR2.

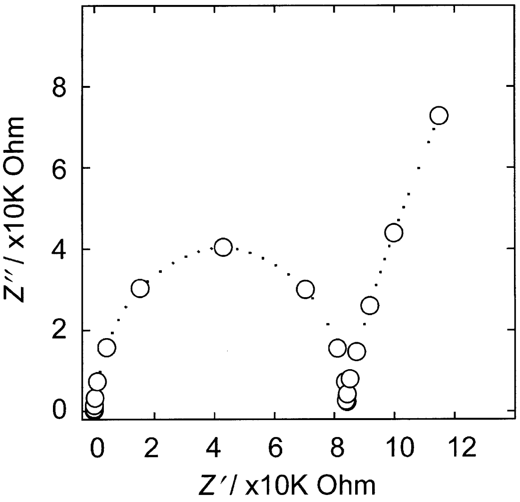

Fig. 6. Cole–Cole plot of DEDPNR3 mixed with LiTFSI salt 20 w/w% at 323 K.

part of impedance, Z'', was dependent upon the real part, Z', to form a half circle. Thus, the bulk resistance (R_b) was determined to be a point of intersection of the curve and axis of abscissa [14]. An ionic conductivity, estimated from R_b, is shown in Fig. 7, as a function of reciprocal temperature. The ionic conductivity of DEDPNR3 mixed with 20 w/w% LiTFSI salt increased as the temperature rose. The ionic conductivity was about 1.98×10^{-6} S cm^{-1} at 323 K, corresponding to that of polyether [15,16]. This demonstrates the possibility of DEDPNR as a SPE due to high polarity and mobility, necessary for the SPE.

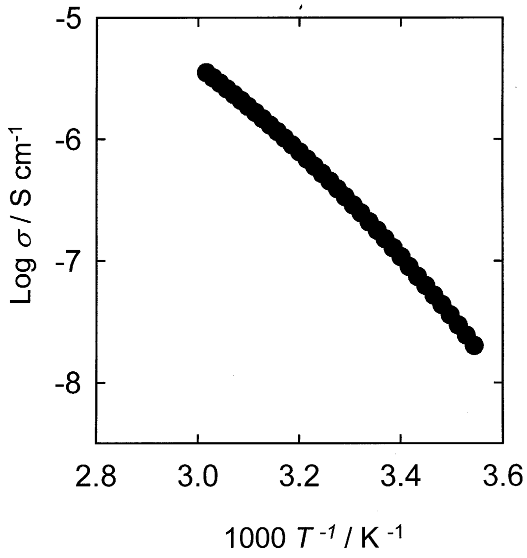

Fig. 7. Temperature dependence of the ionic conductivity of DEDPNR3 mixed with LiTFSI 20 w/w%.

4. Conclusions

The depolymerized natural rubber having epoxy group, prepared by epoxidation of enzymatically DPNR latex, followed by oxidative depolymerization, was found to have low T_g, low M_n and well-defined terminal groups, i.e. aldehyde and α-β unsaturated carbonyl groups. The ionic conductivity of the resulting rubber was 1.98×10^{-6} S cm^{-1} at 323 K, reflecting its high polarity and mobility. This demonstrates the possibility of DEDPNR as a SPE.

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