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Effect of LiBr Concentration on Carbonation of Natural Rubber with Supercritical Carbon Dioxide

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ABSTRACT: The effect of LiBr concentration on carbonation of natural rubber was investigated in relation to the miscibility of LiBr and liquid deproteinized natural rubber having an epoxy group (LEDPNR) as a source. LEDPNR was prepared by epoxidation of deproteinized natural rubber with peracetic acid followed by depolymerization with ammonium persulfate. It was incubated with supercritical carbon dioxide at 403 K for 6 h, after mixing with various amounts of LiBr. The products were characterized through ^{1}H NMR, ^{13}C NMR, two-dimensional correlation spectroscopy (COSY), and two-dimensional heteronuclear correlation (HETCOR) spectroscopy. The conversion and the carbonate unit content of the products were associated with the LiBr concentration. The effect of LiBr concentration on the carbonation of natural rubber was interpreted separately in the miscible state and immiscible state.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique to characterize novel functional polymers. The characterization may be performed after careful assignments of signals appearing in NMR spectrum. Furthermore, conversion, component, and stereoregularity of the polymers are analyzed on the basis of the assignment in regard to reaction conditions. In the present work, the effect of LiBr concentration on carbonation of natural rubber with supercritical carbon dioxide to prepare carbonated natural rubber was investigated through NMR spectroscopy.

Carbonated natural rubber is an artificial green polymer, which is essentially made of carbon dioxide as a source, since the rubber is prepared by biosynthesis occurring in *Hevea brasiliensis* followed by a reaction with carbon dioxide. It may be anticipated to be a functional organic material, whose polarity may vary with carbonate unit content, as shown in Figure 1. To prepare the carbonated natural rubber, it may be possible to apply the proposed organic reaction on alkyl oxirane to natural rubber,[1−4] since natural rubber consists of *cis*-1,4-isoprene units, which may be converted to an epoxy group.[5−8]

Low molecular weight carbonated compounds have been prepared from alkyloxirane with carbon dioxide in the presence of lithium bromide (LiBr) as a catalyst.[1−4] The carbonation was proposed to proceed through an intermediate consisting of the alkyloxirane, carbon dioxide, and LiBr followed by backbiting of −OLi to $-CH_2Br-$ to form cyclic carbonate group. According to the mechanism,[3,4] alkyloxirane as a substrate has to be close to both carbon dioxide and LiBr. In order to apply this reaction to polymeric substrate, thus, it is important to introduce an epoxy group into the polymer and mix with carbon dioxide and LiBr. In this regard, we take notice of natural rubber as a substrate, since it is epoxidized and swollen by supercritical carbon dioxide.[9,10]

To prepare the carbonated natural rubber, we have to purify natural rubber to remove proteins, since they cause side reactions preventing high yield of the product.[11] In previous works,[12,13] we reported an efficient purification procedure of natural rubber with urea, since urea is known to change conformations of the proteins through hydrophilic interactions, and it stabilizes the proteins in water.[14] The resulting deproteinized natural rubber, namely, hyper-deproteinized natural rubber, was proved to contain less than 0.005% w/w nitrogen sources. From hyper-deproteinized natural rubber, we prepared liquid deproteinized natural rubber having epoxy groups (LEDPNR),[15] which were attracted with lithium cation of lithium salt in the mixture.[16,17] As the mixture was reacted with supercritical carbon dioxide at higher temperature and pressure, cyclic carbonate groups could be introduced to natural rubber, in which conversion of the epoxy group and carbonate unit content of the product were 37% and 7.2%, respectively.[18] Since the carbonation is expected to be dependent upon LiBr concentration based upon the previous work on carbonation of alkyloxirane, as reported by Kihara and co-workers,[4] it is important to determine a suitable LiBr concentration for the preparation of carbonated natural rubber.

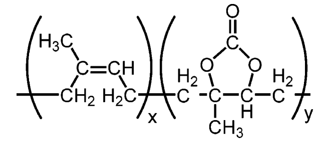

Figure 1. Chemical structure of carbonated natural rubber.

In the present study, the carbonation of liquid epoxidized natural rubber with supercritical carbon dioxide was performed at various LiBr concentrations. The product was characterized by DSC measurement, ^{1}H NMR, ^{13}C NMR, two-dimensional correlation spectroscopy (COSY), and two-dimensional heteronuclear correlation (HETCOR) spectroscopy.

Experimental Section

Natural rubber latex used in this study was commercial high ammonia natural rubber latex. Deproteinization of natural rubber was made by incubation of the latex with 0.1% w/v urea (Nacalai tesque Inc., 99.5%) and 1.0% w/v sodium dodecyl sulfate (Kishida Reagents Chemicals Co. Ltd., 99%) for 1 h at 303 K followed by centrifugation at $10^{4}g$.[5,6] Number-average molecular weight, M_n, weight-average molecular weight, M_w, M_w/M_n, and gel content for

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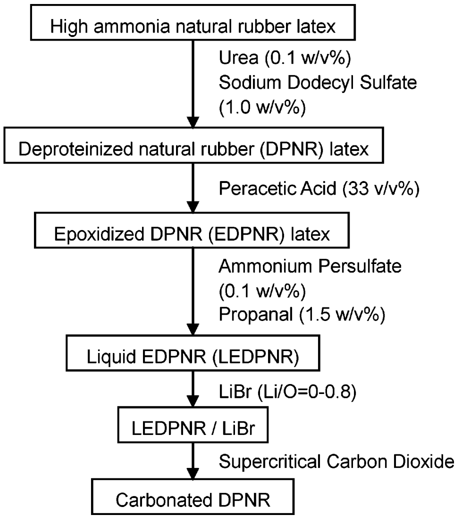

Figure 2. Schematic illustration of preparing carbonated DPNR.

Table 1. M_n**,** M_w**,** M_w/M_n**, and Gel Content of DPNR, EDPNR, and LEDPNR**

specimen	$M_n/10^5$ (g mol^{-1})	$M_w/10^5$ (g mol^{-1})	M_w/M_n	gel content (% w/w)
DPNR	4.2	15.8	3.7	60.8
EDPNR	2.1	5.4	2.6	80.8
LEDPNR	0.21	0.57	2.7	0.0

Table 2. Condition of Carbonation

run no.	LiBr feed (mol/epoxy)	time (h)	temp (K)	pressure (MPa)
1	0.0	6	403	20
2	0.1	6	403	20
3	0.2	6	403	20
4	0.4	6	403	20
5	0.6	6	403	20
6	0.8	6	403	20

the resulting deproteinized natural rubber (DPNR) are tabulated in Table 1.

DPNR, precooled at 283 K, was epoxidized with fresh peracetic acid (33% v/v concentration) in the latex stage for 3 h at pH 5−6. After completion of the reaction, pH of the latex was adjusted to 7.1, and a part of rubber was coagulated by adding an excess of methanol. The resulting epoxidized DPNR (EDPNR) was soaked in water for a day and dried under reduced pressure at 303 K for a week.

Depolymerization of the EDPNR was carried out by incubation of the EDPNR latex with 0.1% w/v ammonium persulfate (Nacalai tesque Inc., 99.5%) and 1.5% w/v propanal (Nacalai tesque Inc., 99.5%) at 338 K for 10 h to prepare LEDPNR latex. The LEDPNR latex was coagulated with excess amount of methanol (Nacalai tesque Inc., 99%) followed by purification with toluene (Nacalai tesque Inc., 99.5%) and methanol, and the coagulated LEDPNR was dried at 303 K for a week under reduced pressure.

LEDPNR was dissolved into THF (Nacalai tesque Inc., 99.5%) followed by mixing it with various LiBr concentrations, as shown in Table 2. From the solution, as-cast films were prepared and dried under reduced pressure for a week. The resulting as-cast films were placed in a high-pressure reactor and reacted with supercritical carbon dioxide at 403 K and 20 MPa for 6 h.

The procedure to prepare the carbonated DPNR is schematically represented in Figure 2.

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 10^4g for 30 min and dried at room temperature for a week under reduced pressure. The gel content, C_{gel}, was estimated, as in the following equation:

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

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

Apparent molecular weights and molecular weight distribution, M_w/M_n, of the rubbers were determined by SEC system of Tosoh Ltd. with a computer-controlled dual pump, a RI-8012 differential refractive index detector, a UV-8011 ultraviolet spectroscopic detector, and a series of three G4000H$_{HR}$ columns (bead size 5 μm, exclusion molecular weight of 400K for polystyrene) or a series of three G6000H$_{HR}$ columns (bead size 5 μm, exclusion molecular weight of 4000K for polystyrene) with 300 mm length and 7.8 mm i.d. each. THF was used as an eluent, and flow rate was 0.5 mL/min at room temperature. Standard polystyrenes were used for calibration.

DSC measurements of LEDPNR/LiBr mixtures and the carbonated DPNR were performed 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. Glass transition temperature, T_g, of the samples was determined from the point of inflection in DSC curve.

NMR measurements were carried out using a JEOL ECA-400 NMR spectrometer operating at 399.65 and 100.4 MHz for ^{1}H and ^{13}C, respectively. The polymer was dissolved into chloroform-*d* without tetramethylsilane (TMS) to make 2% w/v solution for ^{1}H NMR and 20% w/v solution for ^{13}C NMR spectroscopy. Chemical shifts were referred to chloroform in chloroform-*d*. ^{1}H and ^{13}C NMR measurements were carried out at 323 K at the pulse repetition time of 7 and 5 s, the pulse width of 6.1 and 5.0 μs, and pulse delay of 4.24 and 3.79 s, respectively. Two-dimensional COSY and HETCOR measurements were made to collect two-dimensional hypercomplex data. After weighing with shifted sine-bell function, the data was Fourier-transformed in the absolute value mode.

Morphology of the LEDPNR/LiBr mixture was observed by optical light microscopy, using a Nikon ECLIPSE E600 POL microscope equipped with CCD color digital camera module (SONY DFW-SX900). LEDPNR/LiBr mixtures, sandwiched between two cover glasses, were placed on a heating stage (Linkam LK 600PM) whose temperature control was maintained within 0.1 K. The samples were heated to 403 K at a heating rate of 10 K/min. At 403 K, the photomicrograph of the samples was taken with the CCD color digital camera module.

Results and Discussion

Table 1 shows gel contents of DPNR, EDPNR, and LEDPNR. The gel content of EDPNR was 80.8%, which was higher than that of DPNR. The higher value of the gel content of EDPNR, compared with that of DPNR, may be due to the formation of the three-dimensional networks during epoxidation.[19] In order to obtain homogeneous mixture of EDPNR with LiBr, it is required to decompose the three-dimensional networks. In the present study, thus, depolymerization of EDPNR was performed with ammonium persulfate to prepare LEDPNR. After depolymerizing EDPNR to LEDPNR, the gel content was reduced to 0%, reflecting the decomposition of the three-dimensional networks. Figure 3 shows SEC curves for soluble fractions of DPNR, EDPNR, and LEDPNR. A distribution of molecular weight of DPNR was bimodal and unsymmetrical, as reported in the previous paper.[20] After epoxidation of DPNR, the distribution was brought down into unimodal and symmetrical, since higher molecular weight fractions of EDPNR were used for the formation of the gel fraction, which was removed before the SEC measurement. The distribution of LEDPNR was also unimodal and symmetrical, but it appeared at lower molecular weight region. Number-average molecular weight, M_n, weight-average molecular weight, M_w, and polydispersity index, M_w/M_n, were calculated from the SEC curves using a calibration

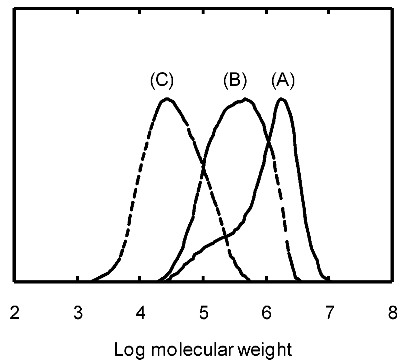

Figure 3. SEC curves for (A) DPNR, (B) EDPNR, and (C) LEDPNR.

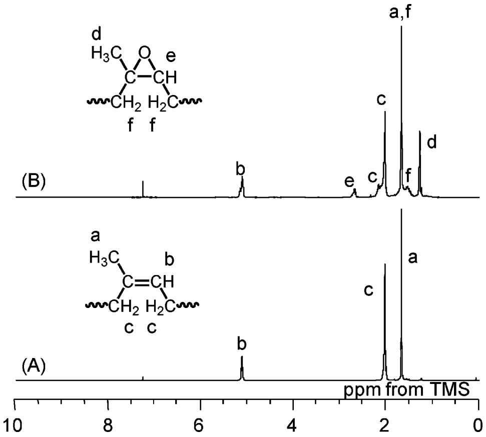

Figure 4. ^{1}H NMR spectra for (A) DPNR and (B) LEDPNR.

curve with standard polystyrene. The estimated values of M_n, M_w, and M_w/M_n for DPNR, EDPNR, and LEDPNR are tabulated in Table 1. The values of M_n, M_w, and M_w/M_n for EDPNR were lower than those for DPNR due to the removal of high molecular weight fraction. After depolymerization of EDPNR, M_n and M_w were reduced to one-tenth of those of EDPNR, while M_w/M_n was similar to that of EDPNR.

Figure 4 shows ^{1}H NMR spectra for DPNR and LEDPNR. In the spectrum for DPNR, signals characteristic of methyl, methylene, and unsaturated methine protons of *cis*-1,4-isoprene unit appeared at 1.7, 2.1, and 5.1 ppm, respectively. After epoxidation and depolymerization of DPNR, other signals appeared at about 1.28, 1.5, 2.2, and 2.7 ppm. The signals were assigned, as shown in Figure 4, according to the previous work:[21] (d) methyl protons of epoxidized isoprene unit, (e) methine proton of epoxidized isoprene unit, and (f) methylene protons of isoprene unit. The epoxy group content of LEDPNR, X_{epoxy}, was estimated from intensity ratio of the signals at 2.7 and 5.1 ppm, as in the following equation:

$$X_{\text{epoxy}} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100 \qquad (1)$$

where I is the intensity ratio of the signals and subscript numbers represent chemical shift (ppm). The estimated epoxy group content of LEDPNR was 33%.

Figure 5 shows DSC thermograms for LEDPNR and LEDPNR/LiBr mixtures, in which the heat capacity fell around a glass transition region in the thermograms. The temperature at which glass transition took place was dependent upon the LiBr concentration. The rise in the temperature may be explained to be due to formation of pseudo-cross-linking junction consisting of an epoxy group of LEDPNR and Li$^+$, as in the case of LEDPNR/lithium bis(trifluoromethanesulfonyl)imide.[16,17] Since interaction between epoxy group and Li$^+$ was suggested, LEDPNR/LiBr mixtures were incubated with supercritical carbon dioxide at 403 K and 20 MPa for 6 h to prepare carbonated natural rubber. Figure 6 shows DSC thermograms for LEDPNR and the resulting carbonated products. After the reaction of LEDPNR with supercritical carbon dioxide, the glass transition occurred at higher temperature region. To investigate the effect of LiBr concentration on the glass transition of the rubber, quantitatively, the glass transition temperature, T_g, was determined from the point of inflection in the curve. A plot of T_g of the carbonated products vs LiBr concentration is shown in Figure 7. The values of T_g of the carbonated products were dependent upon the LiBr concentrations and showed a maximum at Li/O = 0.2.

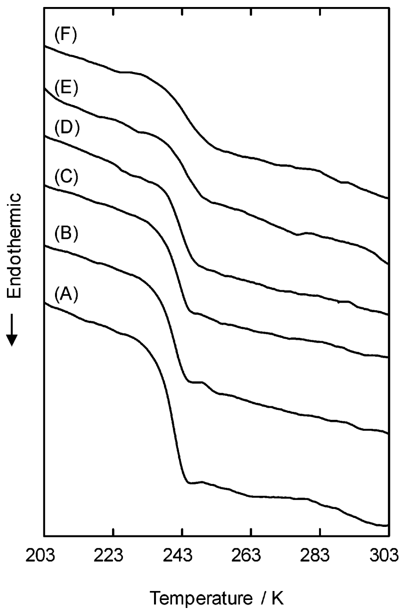

Figure 5. DSC thermograms for (A) LEDPNR and LEDPNR/LiBr at (B) Li/O = 0.1, (C) Li/O = 0.2, (D) Li/O = 0.4, (E) Li/O = 0.6, and (F) Li/O = 0.8.

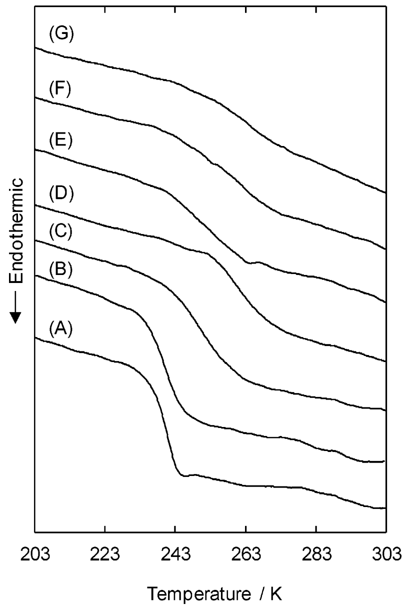

Figure 6. DSC thermograms for (A) LEDPNR and carbonated DPNR prepared in the presence of LiBr at (B) Li/O = 0, (C) Li/O = 0.1, (D) Li/O = 0.2, (E) Li/O = 0.4, (F) Li/O = 0.6, and (G) Li/O = 0.8.

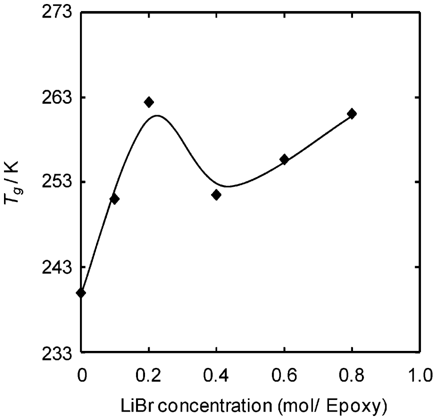

Figure 7. T_g of the carbonated DPNR vs LiBr concentration.

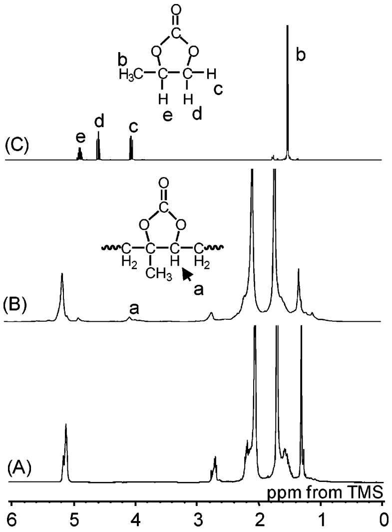

Figure 8. Typical ^{1}H NMR spectra for (A) LEDPNR, (B) carbonated DPNR, and (C) propylene carbonate.

To investigate the change in the T_g, a structural characterization of the products was carried out by NMR spectroscopy. Figure 8 shows a typical ^{1}H NMR spectrum for the carbonated product, together with the spectra for LEDPNR and propylene carbonate as a model. As for the carbonated product, two signals appeared at 4.0 and 4.8 ppm in the spectrum, which did not appear in the spectrum for LEDPNR. For propylene carbonate, two signals at 4.0 and 4.6 ppm have been assigned to equatorial and axial methylene protons of cyclic carbonate group due to interactions with $-CH_3$ and $-H$, respectively.[22] Thus, the signal at 4.0 ppm for the carbonated product can be assigned to the methine proton of the cyclic carbonate group of the cyclic carbonated DPNR. The assignment was supported by COSY measurement of the carbonated DPNR. Two-dimensional COSY spectra for the carbonated DPNR are shown in Figure 9, in which cross peaks appeared due to spin couplings between ^{1}H and ^{1}H. The signal at 4.0 ppm was correlated to the methylene protons at about 1.5 ppm,[18,23,24] which is neighboring with the carbonate group. On the basis of the structure of the carbonated DPNR shown in Figure 1, it may be possible to assign the signal at 4.0 ppm to the methine proton of the cyclic carbonate group.

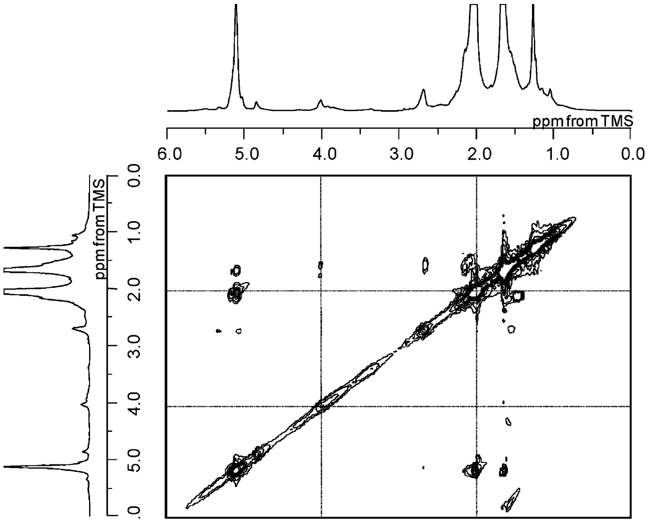

Figure 9. COSY spectra for carbonated DPNR.

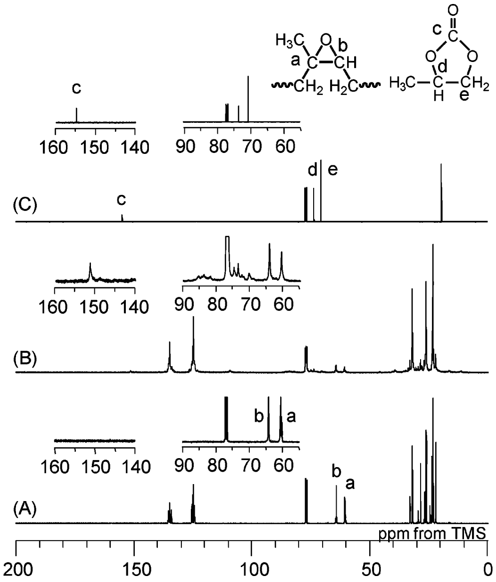

Figure 10. Typical ^{13}C NMR spectra for (A) LEDPNR, (B) carbonated DPNR, and (C) propylene carbonate.

Figure 10 shows typical ^{13}C NMR spectra for LEDPNR, carbonated DPNR, and propylene carbonate. As for LEDPNR, two signals characteristic of the epoxy group were shown at 61 and 64 ppm in the spectrum, which were assigned to quaternary and tertiary carbons of the epoxy group, respectively. But, no signal appeared around 75 and 150 ppm. After carbonation, signals appeared at 74, 75, and 151 ppm, while the intensity of the signals at 61 and 64 ppm decreased. The signals appeared at 74, 75, and 151 ppm were assigned to quaternary ($>C<$), tertiary ($>CH-$), and quaternary ($-O-(C{=}O)-O-$) carbons of the carbonate group, as shown in Figure 1, according to chemical shift values of signals detected for propylene carbonate as a model.

To confirm the assignments of ^{1}H NMR and ^{13}C NMR spectra, HETCOR measurements were carried out for the carbonated DPNR. Figure 11 shows HETCOR spectra for the carbonated DPNR, in which cross peaks appeared due to spin couplings between ^{13}C and ^{1}H in HETCOR spectra. Since the ^{13}C signal at 75 ppm of the methine group of the carbonate group was directly correlated to the ^{1}H signal at 4.0 ppm, it is proved that the ^{13}C signal at 75 ppm and the ^{1}H signal at 4.0 ppm are assigned to methine carbon and methine proton of the cyclic carbonate group, respectively, as shown in Figure 1. These assignments were supported by two-dimensional heteronuclear multiple bond correlation (HMBC) measurement in the previous work.[18]

Since the signal at 4.0 ppm in the ^{1}H NMR spectrum for carbonated DPNR was proved to be the methine protons of the carbonate group, the conversion of epoxy group, ξ, and the

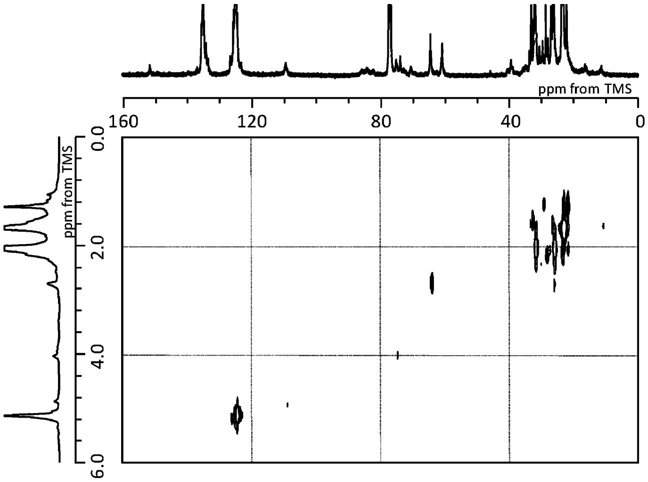

Figure 11. HETCOR spectra for carbonated DPNR.

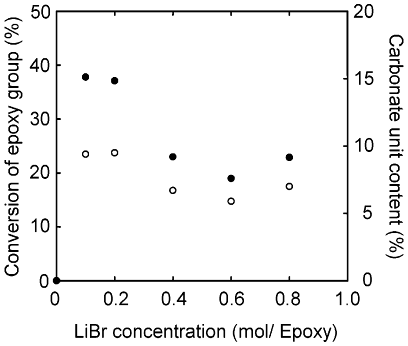

Figure 12. ξ (●) and $X_{\text{carbonate}}$ (○) vs LiBr concentration for carbonated DPNR.

carbonate unit content, $X_{\text{carbonate}}$, for the carbonated DPNR were estimated from the intensity ratio of the signals at 2.7, 4.0, and 5.1 ppm, as in the following equations:

$$\xi = \frac{I_{4.0}}{I_{2.7} + I_{4.0}} \times 100 \tag{2}$$

$$X_{\text{carbonate}} = \frac{I_{4.0}}{I_{2.7} + I_{4.0} + I_{5.1}} \times 100 \tag{3}$$

The estimated values of the ξ and the $X_{\text{carbonate}}$ are shown in Figure 12. The ξ and the $X_{\text{carbonate}}$ were dependent upon the LiBr concentration; that is, they depicted a convex curve with a maximum at Li/O = 0.1 and 0.2, respectively, and they reached to a plateau at Li/O = 0.4. The ξ and the $X_{\text{carbonate}}$ may be concerned with T_g shown in Figure 7. The monotonic increase in the T_g at low LiBr concentration may be expected to be due to a molecular order mixing of LEDPNR and LiBr. The lower value of T_g at Li/O = 0.4 compared with that at Li/O = 0.2 may correspond to the low value of the $X_{\text{carbonate}}$. The decrease in the T_g and the $X_{\text{carbonate}}$ at Li/O = 0.4 may be attributed to the decrease in the effective LiBr concentration useful for the carbonation. Since polarities of LEDPNR and LiBr are different from each other, the decrease in the effective LiBr concentration may be related to phase separation of LEDPNR/LiBr mixture into LEDPNR-rich phase and LiBr-rich phase.

To confirm the phase separation of LEDPNR/LiBr mixture, the morphology of the mixture was observed by optical light microscopy. Figure 13 shows optical light micrographs for LEDPNR/LiBr mixtures prepared at 403 K. The LEDPNR/LiBr mixtures were homogeneous at Li/O = 0.1 and 0.2, reflecting the dissolution of LiBr into LEDPNR. In contrast, droplets appeared in the mixtures at Li/O = 0.4 and 0.6, respectively. This demonstrates that the segregation of LiBr from LEDPNR-rich phase may result in the decrease in the $X_{\text{carbonate}}$, based on the results shown in Figures 7, 12, and 13. The higher values of the ξ and the $X_{\text{carbonate}}$ at Li/O = 0.1 and 0.2 may be explained to be due to a supersaturation of LiBr in LEDPNR, as reported by Youshko and co-workers.[25] Consequently, as long as we use LiBr as a catalyst without any organic solvent, a suitable ratio of LiBr to the epoxy group content was determined to be 0.1–0.2 for the carbonation of LEDPNR.

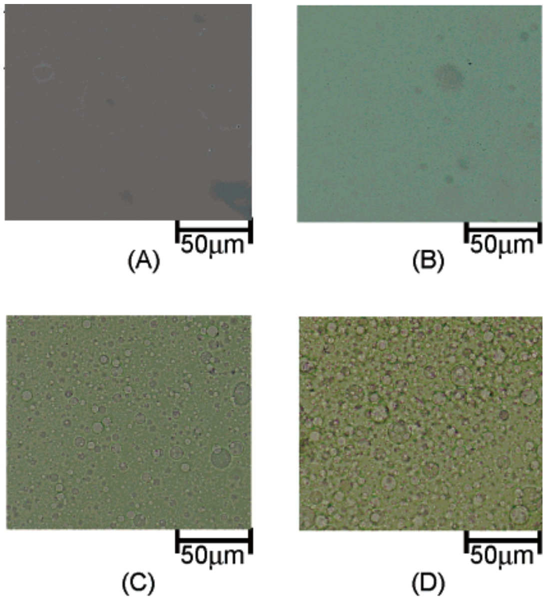

Figure 13. Photomicrograph for LEDPNR/LiBr at (A) Li/O = 0.1, (B) Li/O = 0.2, (C) Li/O = 0.4, and (D) Li/O = 0.6.

In a subsequent paper, we will report some properties of the carbonated DPNR.

Conclusion

The carbonated natural rubber was prepared from LEDPNR with supercritical carbon dioxide in the presence of LiBr. The values of T_g of the resulting carbonated natural rubber were dependent upon the LiBr concentrations. In ^{1}H NMR spectrum for the carbonated natural rubber, a new signal appeared at 4.0 ppm after the carbonation, which was assigned to methine proton of the resulting carbonate group of carbonated natural rubber through 1D- and 2D-NMR spectroscopy. The conversions of epoxy group, ξ, and the carbonate unit content, $X_{\text{carbonate}}$, were dependent upon the LiBr concentration, and they reached maximum at Li/O = 0.1–0.2. On the basis of the morphology observation, the lower value in the ξ and the $X_{\text{carbonate}}$ at higher LiBr concentration may be due to the segregation of LiBr from LEDPNR-rich phase. It is thus concluded that a suitable ratio of LiBr to the epoxy group content was 0.1–0.2 for the carbonation of LEDPNR.

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