Photoreactive Nanomatrix Structure Formed by Graft-Copolymerization of 1,9-Nonandiol Dimethacrylate onto Natural Rubber

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ABSTRACT: Formation of photoreactive nanomatrix structure was investigated by graft-copolymerization of an inclusion complex of 1,9-nonandiol dimethacrylate (NDMA) with β-cyclodextrin (β-CD) onto natural rubber particle using potassium persulfate (KPS), *tert*-butyl hydroperoxide/tetraethylenepentamine (TBHPO/TEPA), cumene hydroperoxide/tetraethylenepentamine (CHPO/TEPA), and benzoyl peroxide (BPO) as an initiator. The graft copolymer was characterized by ^{1}H NMR and FTIR after coagulation. The conversion of NDMA and the amount of residual methacryloyl group were found to be 58.5 w/w % and 1.81 w/w %, respectively, under the suitable condition of the graft-copolymerization. The morphology of the film specimen, prepared from the graft copolymer, was observed by transmission electron microscopy (TEM) after staining the film with OsO_4. Natural rubber particle of about 1.0 μm in diameter was dispersed in poly(NDMA) matrix of about 10 nm in thickness. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2418–2424, 2010

KEYWORDS: graft copolymers; graft-copolymerization; inclusion chemistry; inclusion complex; nanomatrix structure; natural rubber; rubber

INTRODUCTION Photoreactive nanomatrix structure is a novel functional nanophase separated structure, which consists of a dispersoid of major elastomer and a matrix of minor functional polymer having carbon–carbon double bonds as a photoreactive site. The photoreaction of the polymer in the nanomatrix may concrete the nanomatrix structure with not only crosslinking junctions of the elastomer in dispersoid and chemical linkages between the elastomer and the functional polymer but also crosslinking junctions of the functional polymer in the nanomatrix.

In the previous work, we found that the nanomatrix structure played important roles in high proton conductivity of polymer electrolyte membrane[1] and high elastic properties of rubbery material,[2] respectively. However, the resulting electrolyte membrane and the rubbery material were inferior in mechanical properties, such as less tensile strength and low tear energy. This has been explained to be due to no chemical linkages between the functional polymers in the nanomatrix. To improve the properties, it is necessary to introduce crosslinking junctions into the polymers in the nanomatrix, as the chemical linkages between the functional polymers prevent flowing the polymers in the nanomatrix. In this regard, the nanomatrix structure with the photoreactive sites is expected to enhance the mechanical properties after UV-irradiation, which forms a three-dimensional network structure in the nanomatrix.

In our previous work, the nanomatrix structure consisting of a natural rubber particle as the dispersoid of 1 μm in diameter and the functional polymer as the matrix of 15 nm in thickness was formed by coagulating the natural rubber particle covered with grafted functional polymer, such as polystyrene and polymethyl methacrylate.[3–6] Furthermore, the photoreactive rubber latex was prepared in our previous work by graft-copolymerization of an inclusion complex of 1,9-nonandiol dimethacrylate (NDMA) with α-cyclodextrin (α-CD).[7] A methacryloyl group of poly(NDMA) grafted onto the natural rubber particle was confirmed to remain without any reaction, while the other was used for the graft-copolymerization. Based on the results, the photoreactive nanomatrix structure may be formed by coagulating a latex of the photoreactive rubber.

However, the latex was not stabilized during the polymerization, and a part of the reacted rubber particles were coagulated at 52% of conversion. The coagulation has been explained to be due to releasing α-CD from the inclusion complex followed by crosslinking during graft-copolymerization.

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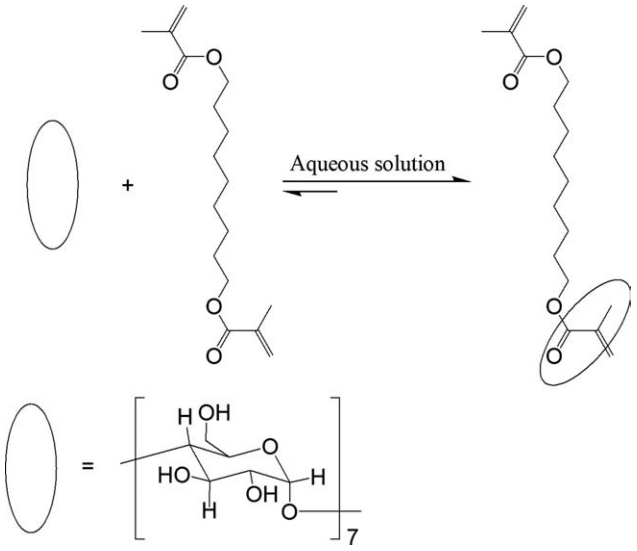

FIGURE 1 Schematic representation for inclusion complex formation of NDMA and β-CD before graft-copolymerization.

In fact, the graft-copolymerization was not completed; that is, the coagulated particles were not covered with poly(NDMA). To cover all particles at high conversion of graft-copolymerization, thus, it is necessary to make a stable inclusion complex. Recently, Ritter and coworkers[8] reported that 1,4-butandiol diacrylate completely penetrated the CD cavity when it formed a complex with methylated β-CD, whereas in the case of 1,4-butandiol dimethacrylate, the CD was located at the terminal end of 1,4-butandiol dimethacrylate. Satav et al.[9] demonstrated that a methacryloyl group of 1,4-butandiol dimethacrylate was protected with β-cyclodextrin (β-CD) having larger cavity of about 6.6 Å in diameter to form the stable inclusion complex. When we use β-CD to form the stable inclusion complex, all particles may be covered with poly(NDMA) to make it possible to form the photoreactive nanomatrix structure which has seen ever.

Here, for the first time, we form the photoreactive nanomatrix structure through graft-copolymerization of the stable inclusion complex prepared with β-CD and NDMA in water (Fig. 1). The formation of the inclusion complex was confirmed by FTIR, solid state ^{13}C NMR, ^{1}H NMR, and X-ray diffraction (XRD). A stability of the inclusion complex was evaluated by determination of solubility product. The resulting inclusion complex was subjected to graft-copolymerization onto natural rubber particle with various radical initiators (Fig. 2). Effects of amount of the inclusion complex and the radical initiator on conversion of NDMA were investigated. The resulting graft copolymer was characterized by ^{1}H NMR, FTIR. The morphology of the graft copolymer was observed by TEM.

EXPERIMENTAL

Materials

Natural rubber latex used in this study was about 60% dry rubber content (DRC) of a commercial high-ammonia natural rubber latex (HANR: Golden Hope, Malaysia). *tert*-Butyl hydroperoxide/tetraethylenepentamine (TBHPO/TEPA), cumene hydroperoxide (CHPO), tetraethylenepentamine (TEPA), and benzoyl peroxide (BPO) were purchased from NOF Corporation. Sodium dodecyl sulfate (SDS, 98%) was purchased from Kishida Chemical Co., Ltd. β-CD, potassium persulfate (KPS, 95%), and chloroform-*d* (99.8%) were purchased from Wako Pure Chemical Industry. Urea (99.5%), methanol (99.5%), acetone (99.5%), and potassium bromide were purchased from Nacalai Tesque, Inc. The reagents were used without further purification.

Deproteinization[10,11]

HANR latex was sieved with a stainless 200 mesh before usage. HANR latex (300 g) placed in a 1 L beaker was diluted with 2.0 w/w % of SDS aqueous solution (300 g) to make 30 w/w % DRC latex before deproteinization. The diluted latex was mixed with urea (0.6 g) and stirred for 1 h at room temperature and it was subjected to centrifugation at 10^4 rpm and 288 K for 30 min to separate the rubber cream fraction from serum fraction. The resulting cream fraction, which mainly contains rubber, was added into 0.5 w/w % of SDS aqueous solution (200 g) in a 1 L beaker. The mixture of the cream fraction and the SDS aqueous solution was stirred slowly at room temperature for 1 h to redisperse the rubber particle. The resulting latex was sieved with a stainless 200 mesh and it was subjected to the centrifugation and the redispersion twice to purify natural rubber. For the last time of redispersion, the concentration of SDS was decreased to be 0.1 w/w % of SDS aqueous solution. The resulting deproteinized natural rubber (DPNR) latex was kept in a 500 mL glass bottle in the dark at room temperature. DRC of the DPNR latex was measured as follows; DPNR latex (2 g) was poured into a small metal container and it was dried in an oven at 323 K until a constant weight was reached. The DRC was estimated from the weight of the latex and dried rubber, as in the following eq. 1:

$$\mathrm{DRC(W/W\ \%)} = \frac{W_{\text{dried rubber}}}{W_{\text{latex}}} \times 100 \qquad (1)$$

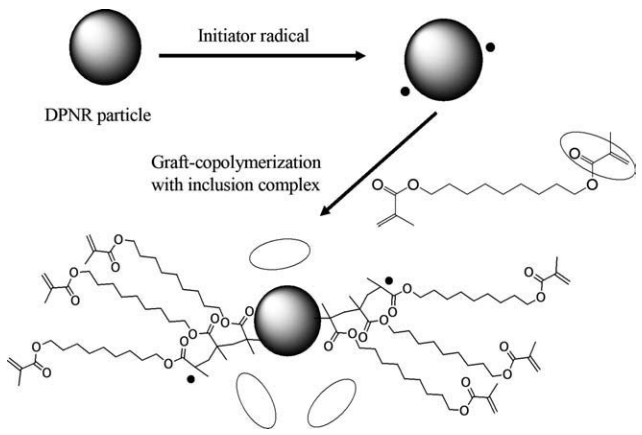

FIGURE 2 Schematic representation for graft-copolymerization of inclusion complex onto DPNR in latex stage.

TABLE 1 Conditions for Inclusion Complex Formation of NDMA and CD

Feed of NDMA (mol)	0.044	0.044	0.044
Feed of β-CD (mol)	0.044	0.044	0.044
Ion-exchanged water (mL)	400	400	400
Reaction temperature (K)	303	323	363
Reaction time (h)	5	5	5

where $W_{\text{dried rubber}}$ and W_{latex} represent the weight of the dried rubber and the latex, respectively.

Preparation of Inclusion Complex

β-CD was dissolved in ion-exchanged water. NDMA as a divinyl monomer was added in stoichiometric amount and the mixture was stirred at 363 K for 1–5 h. The complex was precipitated out from the mixture. The precipitated complex was filtered and it was washed with hot ion-exchanged water to remove uncomplexed β-CD. The crystalline complexes were dried at 323 K for 1 week under reduced pressure. Conditions of inclusion complex formation of NDMA and β-CD are tabulated in Table 1.

Determination of Solubility Product

The inclusion complex (0.3 mmol) was suspended into water (10 mL). The suspension was shaken for 1 h at 30 °C, and allowed to stand for 1 h at 30 °C. After filtration of the supernatant, the filtrate was dried at 50 °C under reduced pressure to give free CD, which was identified with ^{1}H NMR measurement. The solubility product was determined by the concentration of free CD estimated by gravimetric method.

Graft-Copolymerization

Graft-copolymerization of the inclusion complex onto DPNR was carried out with a radical initiator. DPNR latex (500 g, 20 w/w % DRC) was charged with N_2 gas. Initiator and the complex were added to the latex, respectively. The reaction was carried out by stirring the latex at about 400 rpm for 2 h at 343 K. The unreacted NDMA was removed by using a centrifuge. The as-prepared graft copolymer (gross polymer) was obtained by dipping a glass tube into the reacted latex and dried under reduced pressure at ambient temperature for more than a week. The gross polymer was extracted with acetone in a Soxhlet apparatus under nitrogen atmosphere in the dark and dried under reduced pressure for a week, in which the removal of almost all free-polymer, isolated from natural rubber, was completed by the extraction for 24 h. Conditions of graft-copolymerization of inclusion complex onto DPNR in latex stage are tabulated in Table 2.

Characterization

FTIR measurement was carried out using a JASCO FT-IR 410 spectrometer with a resolution of 4 cm^{-1}. The sample was mixed with potassium bromide powder in the ratio of 5 to 95 w/w %. The mixture was grinded in the mortar and it was casted into a DR-81 diffusive reflection attachment.

NMR measurements were carried out using a JEOL EX-400 NMR spectrometer operating at 399.65 and 100.4 MHz for ^{1}H and ^{13}C, respectively. The sample was dissolved into chloroform-d or dimethyl sulfoxide-d_6 (DMSO-d_6) without tetramethylsilane. Chemical shifts were referred to chloroform in chloroform-d or to DMSO in DMSO-d_6. ^{1}H and ^{13}C NMR measurements were carried out at 323 and 298 K at the pulse repetition time of 7 and 5 s, respectively.

Solid state ^{13}C CP/MAS NMR measurements were carried out with a JEOL ECA-400 NMR spectrometer at room temperature with spin rate of 7 MHz, scan time of 1000 times and contact time of 1 s. Hexamethylbenzene was used for reference. Before measurement, samples were crushed by JFC-300 cryogenic sample crusher.

Crystallinity changes in the complex formation of NDMA with β-CD were confirmed by Mac Science MXP03HF22 X-ray powder diffraction and image-plate photography using graphite monomchromator with a voltage of 40 kV and a current of 35 mA. The diffractogram was recorded in the 2θ angle range between 5 and 70°.

Observation of morphology for the graft copolymer was made with TEM, JEOL JEM-2100 at accelerating voltage of 200 kV. The ultra thin sections of the graft copolymer were prepared by a microtome (Ultracut N, Reichert-Nissei FC S) at a temperature lower than T_g of NR. The thin sections with the thickness of about 100 nm were stained by OsO_4 at room temperature for 5 min.

TABLE 2 Various Conditions of Graft-Copolymerization of Inclusion Complex onto DPNR in Latex Stage

No.	Complex (g/kg-Rubber)	Initiator	(mol/kg-Rubber)	Reaction Temp. (K)	NDMA Content (w/w %)	NDMA Conversion (w/w %)
1	150	KPS	0.033	353	1.38	44.4
2	150	CHPO/TEPA	0.033	313	0.06	2.1
3	150	BPO	0.033	353	0.25	8.1
4	150	TBHPO/TEPA	0.033	303	1.81	58.5
5	150	TBHPO/TEPA	0.01	303	0.85	27.3
6	150	TBHPO/TEPA	0.1	303	1.73	55.6
7	50	TBHPO/TEPA	0.033	303	0.71	69.0
8	300	TBHPO/TEPA	0.033	303	1.87	30.1

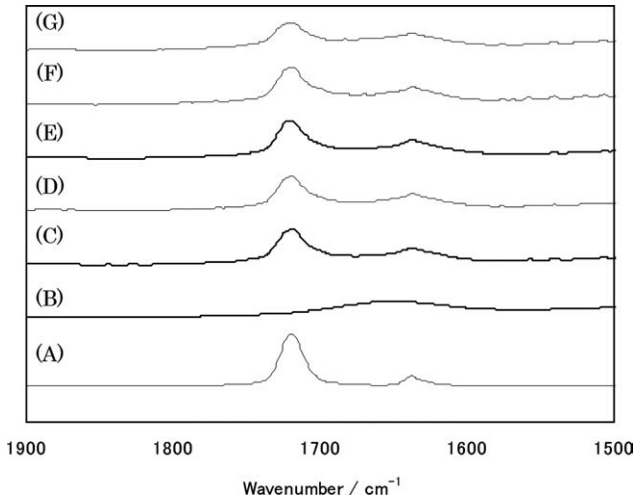

FIGURE 3 FTIR spectra for (A) NDMA, (B) β-CD, inclusion complex of β-CD and NDMA prepared at 363 K for (C) 1 h, (D) 2 h, (E) 3 h, (F) 4 h, and (G) 5 h.

RESULTS AND DISCUSSION

Inclusion Complex Formation of NDMA and β-CD

Figure 3 shows FTIR spectra ranging from 1500 to 1900 cm^{-1} for NDMA, β-CD and the inclusion complex of NDMA with β-CD prepared at 363 K for 1–5 h, respectively. The spectrum of the inclusion complex showed a broad peak at about 1640 cm^{-1}, whereas the corresponding β-CD peak appeared at about 1649 cm^{-1}. This may be attributed to the interaction of NDMA within β-CD cavity.[12–15] As for NDMA, a stretching vibration peak of carbon–carbon double bond and carbonyl group appeared at about 1640 and 1719 cm^{-1}, respectively. After forming the inclusion complex of NDMA with β-CD, the peak height at 1719 cm^{-1} decreased with reaction time, while that at 1640 cm^{-1} did not vary. The decrease in the peak height at 1719 cm^{-1} may be explained to be due to the interaction between carbonyl group of NDMA and β-CD at longer reaction time. The percentage of the complex formation was estimated from a ratio of peak height at 1719 cm^{-1} to that at 1640 cm^{-1}, as in the following eq. 2:

$$\text{Complex formation } (\%) = \frac{(I_{C=O}/I_{C=C})_{\text{Monomer}} - (I_{C=O}/I_{C=C})_{\text{Inclusion complex}}}{(I_{C=O}/I_{C=C})_{\text{Monomer}}} \times 100 \quad (2)$$

where $I_{C=O}$ and $I_{C=C}$ are peak height of a carbonyl group at 1719 cm^{-1} and a carbon–carbon double bond at 1640 cm^{-1}, respectively.

Figure 4 shows a plot of percentage of complex formation versus reaction time at various temperatures. The complex formation of NDMA with β-CD increased with increasing reaction time. Figure 4 also shows the effect of temperature on the complex formation. An ability to form the complex at 363 K was higher than those at 303 and 323 K. This may be attributed to higher solubility of NDMA into water at higher

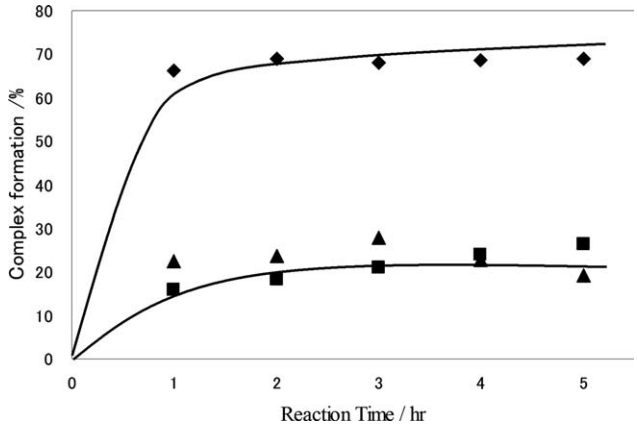

FIGURE 4 Plot of percentage of complex formation versus reaction time for the inclusion complex at various temperatures; (■) 302 K, (▲) 323 K, and (◆) 363 K.

temperature. The inclusion complex prepared from NDMA and β-CD at 363 K for 5 h was subjected to solid state ^{13}C NMR, XRD, and ^{1}H NMR measurements.

Solid state ^{13}C CP/MAS NMR spectra for the inclusion complex and β-CD is shown in Figure 5. In the spectrum of β-CD, four signals characteristic of C_6, C_2, C_3, C_5, C_4, and C_1 of β-CD appeared at 62.2, 70–75, 81.0, and 102.2 ppm. Each signal was observed as an overlapped signal due to each carbon of glucose unit. After forming the inclusion complex, the spectrum showed apparent single signals for each carbon of glucose unit accompanying signals of NDMA, which were assigned as shown in Figure 5. It is well known that β-CD retains less symmetrical cyclic conformation when it does not include any guest into the cavity.[16–21] In contrast, apparent single signals for each carbon of glucose unit of β-CD in the inclusion complex indicate that symmetrical cyclic conformation of β-CD is formed, that is, same environment for each glucose unit of β-CD due to formation of the inclusion complex.

Figure 6 shows XRD patterns for β-CD and the inclusion complex, respectively. The XRD pattern of β-CD was distinguished from that of the inclusion complex. The difference in XRD

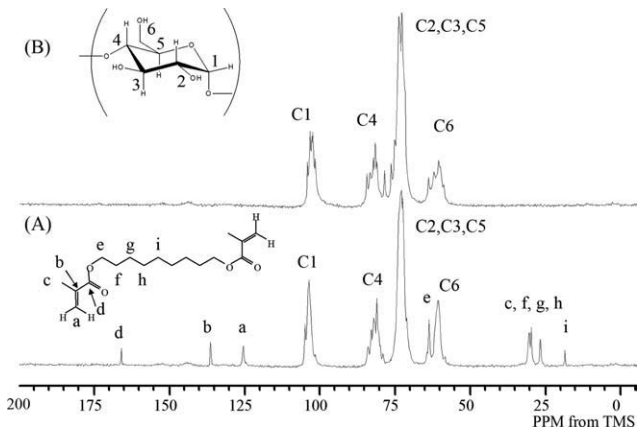

FIGURE 5 ^{13}C CP/MAS NMR spectra for (A) inclusion complex and (B) β-CD.

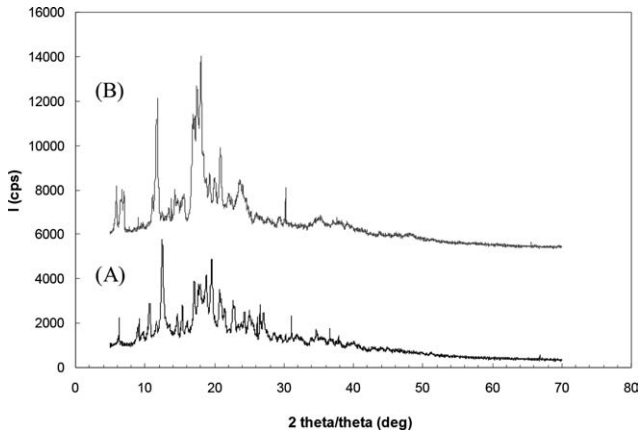

FIGURE 6 XRD diffractograms for (A) β-CD and (B) inclusion complex.

pattern may indicate a change in crystalline form due to the formation of the inclusion complex. The main peaks for β-CD appeared at $2\theta = 12.2°$, 14.3°, 21.8°, and 22.7°, which indicate a cage-type packing, whereas inclusion complex showed new peaks at $2\theta = 7.6°$, 11.3°, 12.8°, 16.8°, 20.1°, and 33.16° accompanying disappearance of the main peaks for native β-CD. As is well known, the peak at $2\theta = 7.6°$ and 20.1° in the inclusion complex is characteristic for the channel structure of β-CD including long guest molecules and polymers in particular.[9,12,19–24] Furthermore, the absence of uncomplexed β-CD was confirmed in the inclusion complex as there is no peaks of β-CD. Therefore, it was demonstrated that the inclusion complex was formed with NDMA and β-CD.

To determine a ratio of NDMA and β-CD, ^{1}H NMR spectra for NDMA, the inclusion complex, and β-CD were measured in DMSO-d_6 as shown in Figure 7.[9] Six signals for NDMA and five signals for β-CD appeared in the ^{1}H NMR spectra, respectively. These signals were assigned as shown in Figure 7, according to the previous literature.[9] After forming the inclusion complex, all signals in ^{1}H NMR spectrum were attributed to those of β-CD and NDMA. To estimate a ratio of NDMA and β-CD in the inclusion complex, integration of the

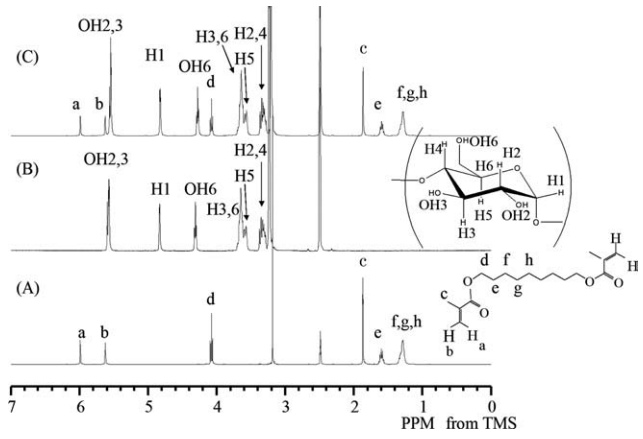

FIGURE 7 ^{1}H NMR spectra for (A) NDMA monomer, (B) β-CD, and (C) inclusion complex (solvent: DMSO-d_6).

peak at 4.1 ppm corresponding to four protons of methylene group adjacent to methacryloyloxy group of NDMA (—OCH_2—) was compared with the peak at 4.82 ppm corresponding to seven protons of methine group in β-CD (H1), although NDMA might be released from β-CD in DMSO-d_6. The integration showed a ratio of 1:1 of NDMA and β-CD in the inclusion complex. This suggests that the inclusion complex was formed in a ratio of 1:1.

To evaluate the complex stability, a solubility product of the resulting inclusion complex, which was difficult to dissolve into water, was compared with the inclusion complex of NDMA with α-CD prepared in our previous study.[7] The solubility product (K_{sp}) at an equilibrium state is expressed as follows:

$$\begin{aligned} &\mathrm{CD \cdot NMDA} \rightleftharpoons \mathrm{CD + NDMA} \\ &K_{sp} = [\mathrm{CD}][\mathrm{NDMA}] \end{aligned} \tag{3}$$

where [CD] and [NDMA] are concentration of CD and NDMA dissociated from the inclusion complex in water, respectively. eq. 3 is converted to eq. 4, as the inclusion complex was formed in a ratio of 1:1.

$$K_{sp} = [\mathrm{CD}]^2 \tag{4}$$

The estimated K_{sp} for the inclusion complex with β-CD and α-CD in water were 1.16×10^{-6} and 3.29×10^{-6}, respectively. This result indicates that the inclusion complex with β-CD was more stable than that with α-CD in water.

Graft-Copolymerization of Inclusion Complex onto DPNR Particle

Before graft-copolymerization, natural rubber latex was purified to mainly remove protein which is well known as radical scavenger to disturb graft-polymerization.[25] Figure 8

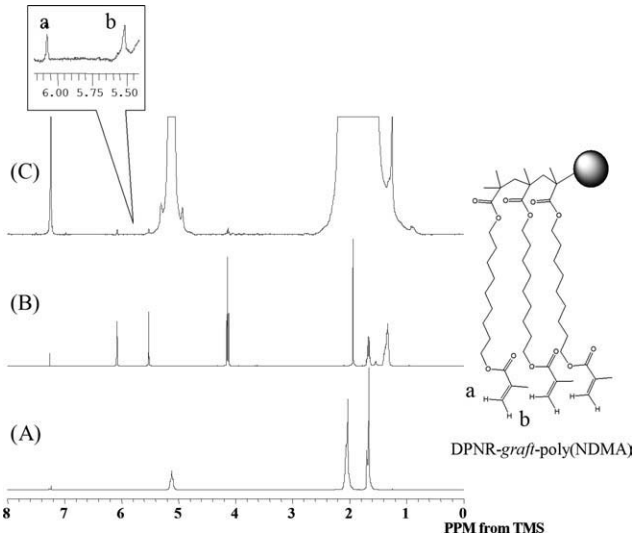

FIGURE 8 ^{1}H NMR spectra for (A) DPNR, (B) NDMA, and (C) DPNR-*graft*-poly(NDMA) (after acetone extraction) prepared from 20%DRC DPNR, 15% inclusion complex for 3 h at 303 K (solvent: chloroform-*d*).

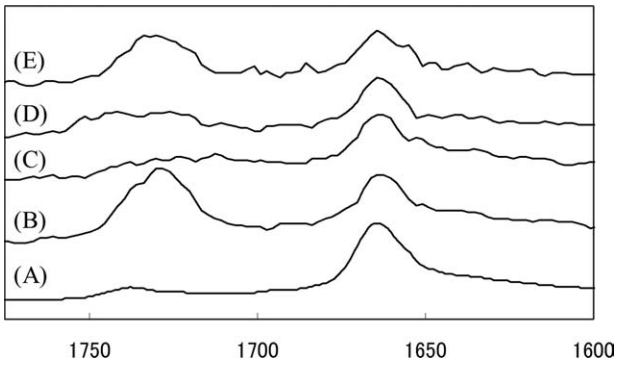

FIGURE 9 FTIR spectra of (A) DPNR, DPNR-*graft*-NDMA copolymer using (B) TBHPO/TEPA, (C) CHPO/TEPA, (D) BPO, and (E) KPS as a initiator.

shows ^{1}H NMR spectra for DPNR, NDMA and graft copolymer (DPNR-*graft*-poly(NDMA)) prepared from 20 w/w % DRC of DPNR latex and 150 g/kg-rubber of the inclusion complex in the presence of 0.033 mol/kg-rubber of TBHPO/TEPA at 303 K for 3 h. Signals in the spectra for DPNR and NDMA were assigned according to the literature.[7] After the graft-copolymerization of the inclusion complex onto DPNR particle, two signals at 5.58 and 6.15 ppm appeared in the spectrum, which were assigned to unsaturated methylene protons of methacryloyl group. As the signals still appeared even after extraction of the graft copolymer with acetone for 24 h, the residual methacryloyl group is considered to link with natural rubber. Thus, amount of residual methacryloyl group after graft-copolymerization was estimated, as in the following eq. 5:

$$\text{Amount of residual methacryloyl group}\,(\%) = \frac{I_{5.58}/(I_{4.10-4.20}/4)_{\text{graft copolymer}}}{I_{5.58}/(I_{4.10-4.20}/4)_{\text{monomer}}} \times 100 \quad (5)$$

where I is the intensity of the signals and subscript numbers represent chemical shift (ppm) of the signals. The estimated value of amount of residual methacryloyl group is 45.3%. This suggests that the formation of the inclusion complex maintained the methacryloyl group of NDMA after graft-copolymerization.

Figure 9 shows FTIR spectra ranging from 1600 to 1800 cm^{-1} for DPNR, DPNR-*graft*-poly(NDMA) prepared with TBHPO/TEPA, CHPO/TEPA, BPO, or KPS as an initiator, respectively. A peak height was normalized with a height of reference peak at 1660 cm^{-1}, which was identified to a stretching vibration of carbon–carbon double bond of natural rubber. As for DPNR-*graft*-poly(NDMA), a stretching vibration peak of carbonyl group of NDMA appeared at 1730 cm^{-1}. A conversion and content of NDMA in DPNR-*graft*-poly(NDMA) were estimated from a ratio of the peak height at 1730 cm^{-1} to that at 1660 cm^{-1} by using a calibration curve.

$$\text{Content of NDMA}\,(\%) = \frac{\text{Weight of NDMA unit in the graft} - \text{copolymer}}{\text{Weight of graft} - \text{copolymer}} \times 100 \quad (6)$$

$$\text{Conversion of NDMA}\,(\%) = \frac{\text{Weight of NDMA unit in the graft} - \text{coplymer}}{\text{Weight of feed of NDMA}} \times 100 \quad (7)$$

Table 2 shows the estimated conversion and content of NDMA. The conversion of NDMA was dependent on initiator, in which the highest conversion, 69.0 w/w %, was accomplished by using 0.033 mol/kg-rubber of TBHPO/TEPA. On the other hand, the conversion of NDMA increased with decreasing feed of the inclusion complex, while the content of NDMA was reached to plateau at feed of 150 g/kg-rubber of inclusion complex. It is quite noteworthy that no coagulation occurred during graft-copolymerization even at higher conversion of more than 58.5%. This may be attributed to formation of the stable inclusion complex between NDMA and β-CD, because β-CD free from NDMA is formed an inclusion complex with SDS, which may coagulate the latex.[26–28] A suitable condition of the graft-copolymerization was

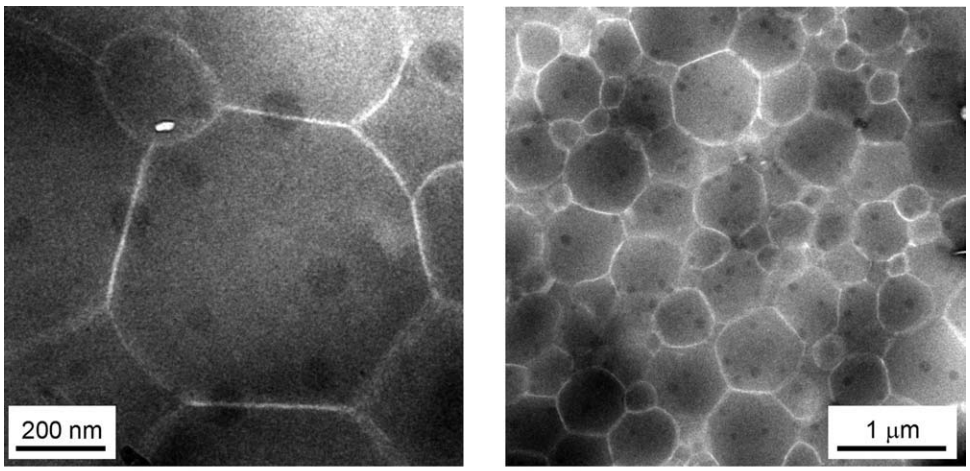

FIGURE 10 TEM photographs for DPNR-*graft*-poly(NDMA), (a): ×20,000, (b): ×5000.

determined to be 150 g/kg-rubber of inclusion complex and 0.033 mol/kg-rubber of TBHPO/TEPA. The resulting product, DPNR-*graft*-poly(NDMA), prepared under suitable condition was subjected to TEM observation.

TEM photographs for DPNR-*graft*-poly(NDMA) are shown in Figure 10, in which a gloomy domain is natural rubber and a bright domain is poly(NDMA). As is clearly seen, the natural rubber particle of about 1.0 μm in diameter was dispersed in poly(NDMA) matrix of 10 nm in thickness to form nanomatrix structure, while it did not contain poly(NDMA). Furthermore, a volume fraction of poly(NDMA) matrix was estimated by image-analysis of the photograph to be about 3 v/v %, which corresponded to 1.81 v/v % estimated from NDMA content shown in Table 2. These results indicate that the graft-copolymerization occurs only on the surface of natural rubber particle. This implies that formation of the inclusion complex changed polarity of hydrophobic NDMA to inhibit penetrating NDMA into hydrophobic natural rubber particle. Consequently, the photoreactive nanomatrix structure was formed in spite of as low as 1.81 w/w % of NDMA content, which has seen ever.

CONCLUSIONS

The photoreactive nanomatrix structure was formed by graft-copolymerization of the stable inclusion complex of NDMA with β-CD onto deproteinized natural rubber. The content, the conversion, and the residual methacryloyl group of NDMA for the graft-copolymerization were 1.81, 58.5, and 45.3%, respectively, at NDMA feed of 150 g/kg-rubber and initiator concentration of 0.033 mol/kg-rubber. TEM observation of the resulting graft copolymer showed that natural rubber particle of about 1.0 μm in diameter was dispersed in poly(NDMA) matrix of 10 nm in thickness.

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