



Latex-state ^{13}C -NMR spectroscopy for poly(butyl acrylate)

Yusuke Iizuka¹ · Yoshimasa Yamamoto² · Seiichi Kawahara¹

Received: 25 April 2018 / Revised: 18 November 2018 / Accepted: 18 November 2018 / Published online: 12 December 2018
© Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract

The resolution and the relaxation time of poly(butyl acrylate) in latex-state ^{13}C -NMR spectroscopy are associated with local motions of the polymer in a dispersoid. Latexes were prepared by emulsion polymerization of butyl acrylate with ammonium persulfate. The latex-state ^{13}C -NMR spectra were measured at 323–353 K with a spectrometer operating at 399.7 and 100.4 MHz for ^1H and ^{13}C , respectively. The half width of the latex-state ^{13}C -NMR spectrum depends on the temperature. The half width and the spin-spin relaxation time, T_2 , are superimposed onto the master curve with a reference temperature, T_X .

Keywords Latex-state ^{13}C -NMR · Poly(butyl acrylate) · Local motion

Introduction

Polymer dynamics have been investigated with respect to various motion relaxations such as α -relaxation, β -relaxation, and γ -relaxation. These are assigned to the segmental motion of the main chain, the local motion of the main chain, and the motion of the pendant groups, respectively [1, 2]. These relaxations are usually investigated via measurements of viscoelastic properties, dielectric constant, and NMR spectra [3]. For instance, the relaxation temperatures of poly(butyl acrylate), PBA, have been determined by dielectric constant measurements. That is, $T_\alpha = 240$ K, $T_\beta = 155$ K [4], and $T_\gamma = 142$ K [1]. However, few studies have examined other relaxation temperatures because some relaxations occur at a very low temperature and they interfere with each other. Consequently, it is important to develop a novel technique to investigate various relaxations over a wide temperature range.

Latex-state NMR spectroscopy is a unique technique to characterize hydrophobic rubbery polymers as a soft material dispersed in water. Since latex is composed of

rubbery polymer particles and water [5, 6], it may allow the mobility of polymers in a particle or the movement of a particle itself in water to be investigated in terms of the resolution of the NMR spectroscopy and relaxation time, which are associated with the magnetic dipole-dipole interaction [7–10]. Considering such application fields, latex-state NMR should become a principal technique to investigate the structure and the dynamics of the rubbery polymers in water.

Previously, we proposed latex-state NMR spectroscopy to characterize crosslinked rubbery polymers present in water [11]. We determined a suitable surfactant concentration and dry rubber content (DRC) of latex for NMR spectroscopy (i.e., 1 w/w% in surfactant concentration and 10 w/w% in DRC). Under suitable conditions, the value of the spin-lattice relaxation time, T_1 , of the polymers in the latex is quite similar to that in the solid but not in the liquid. Additionally, it is independent of the particle size [12].

In contrast, the half width of the latex-state NMR spectrum is identical to that of the solution-state NMR spectrum, and both are narrower than that of the solid-state NMR spectrum. The half width of the latex-state NMR spectrum is expressed as a function of the dispersion coefficient of the Brownian motion of the dispersoid in water. The isomeric unit contents of polybutadiene (i.e., 1,4-*cis*, 1,4-*trans*, and 1,2 unit contents [5]), the crosslinking junctions of natural rubber (i.e., carbon-sulfur linkages [11]), and epoxidized deproteinized natural rubber [13] can be quantitatively analyzed by latex-state NMR spectroscopy.

✉ Seiichi Kawahara
kawahara@mst.nagaokaut.ac.jp

¹ Department of Material Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

² Department of Mechanical Engineering, National Institute of Technology, Tokyo College, 1220-2 Kunugida-machi, Hachioji-shi, Tokyo 193-0997, Japan

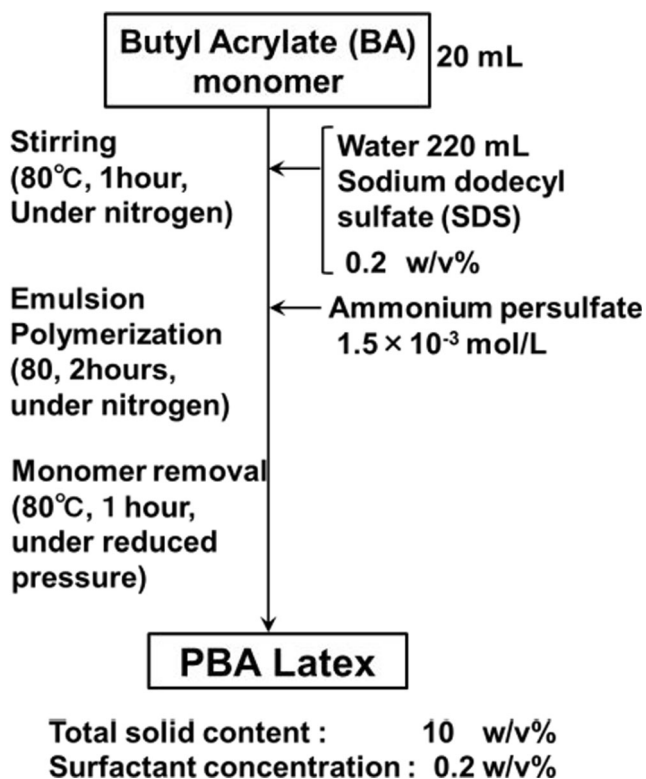


Fig. 1 Overview of the experimental procedure

Latex-state NMR may rely on the active motions of rubbery polymers at an ambient temperature since the glass transition temperature of the polymers is significantly lower, providing a sufficient free volume fraction [14]. In this case, the contributions of the Zeeman term and the dipole-dipole interaction term may be considered in the Hamiltonian expression. When latex in a static magnetic

Table 1 Comparison of the values of the half width of the signals in the solution-state ^{13}C -NMR and latex-state ^{13}C -NMR spectra for PBA

Half width	C7 [Hz]	C6 [Hz]	C5 [Hz]	C4 [Hz]	C3 [Hz]
Solution-state ^{13}C -NMR	8	8	12	28	35
Latex-state ^{13}C -NMR	6	7	12	35	40

field is irradiated with a magnetic pulse, the rubbery polymers in latex have a time-dependent condition due to the rotational movement of the particle. This corresponds to a multi-pulse technique, which may reduce the contribution of the dipole-dipole interaction term in conjunction with the active motions of the rubbery polymers and the rotational movement of the particle. Therefore, the dipole-dipole interaction term may be eliminated in the Hamiltonian expression by not only the active motions of the rubbery polymers but also the rotational movement of the particle.

It is important to realize that the active motions of the rubbery polymer can be distinguished from the rotational movement of the dispersoid. For instance, the active motions of the rubbery polymers are divided into various relaxation modes such as α -relaxation, β -relaxation, γ -relaxation, etc. These modes occur at various temperatures. On the other hand, rotational movements depend on the particle size and may be associated with the spin-spin relaxation time, T_2 , or reciprocal half width, $\nu_{1/2}$, since $\nu_{1/2} = 1/(\pi T_2)$.

Herein the factors influencing the resolution and the relaxation time of latex-state NMR spectroscopy are investigated.

Fig. 2 **a** Latex-state ^{13}C -NMR spectrum for PBA at 353 K and **b** solution-state ^{13}C -NMR spectrum for PBA at 353 K

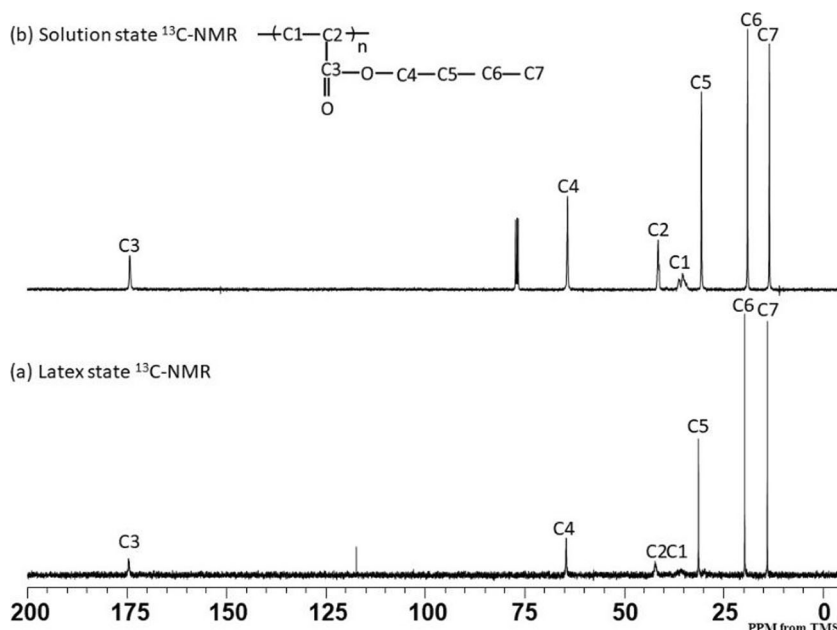


Table 2 Glass transition temperature and volume mean particle diameter for PBA

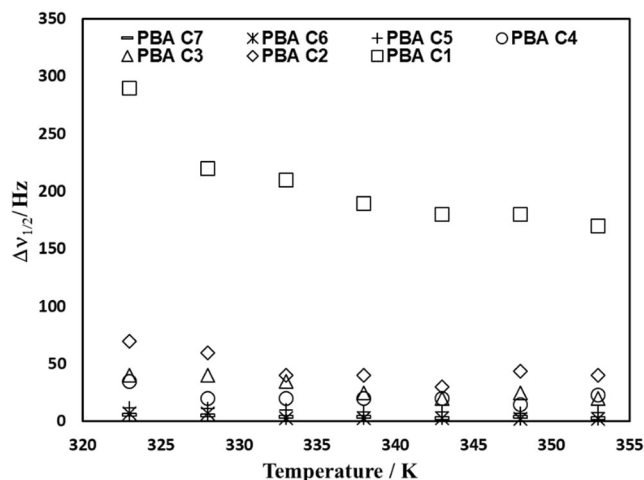
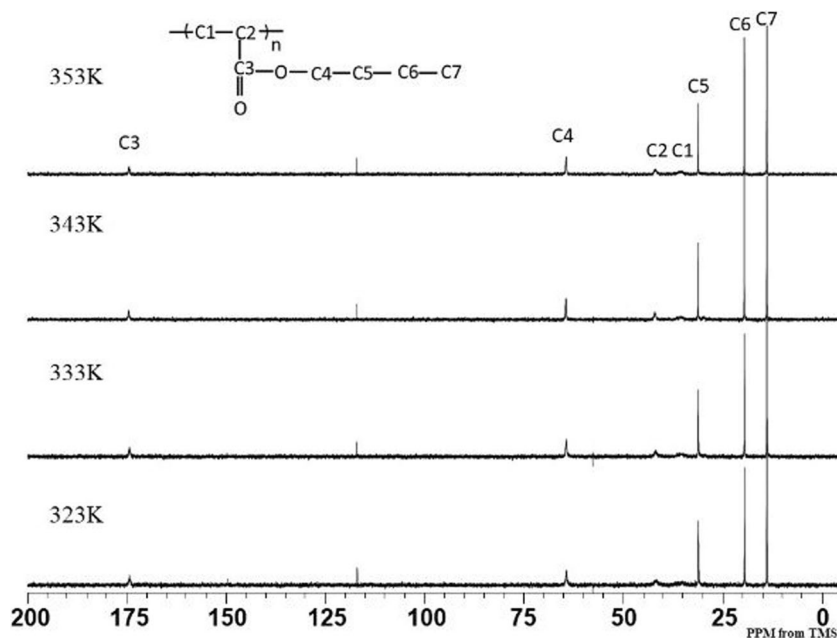
Specimen	Glass transition temperature T_g [°C]	Volume mean particle diameter [nm]
PBA	-47	75

Specifically, the relationship between the local motions of a polymer in a dispersoid and the resolution of latex-state NMR spectroscopy is examined.

Experimental

Material

The monomer, surfactant, and initiator were butyl acrylate (Tokyo Chemical Industry), sodium dodecyl sulfate, and ammonium persulfate (Kishida Reagent Chemical), respectively. The samples were prepared by emulsion polymerization of butyl acrylate in deionized water in the presence of sodium dodecyl sulfate. Butyl acrylate was used as received. The emulsion polymerization of butyl acrylate (0.56 mol/L) was performed with ammonium persulfate (1.5×10^{-3} mol/L) in 220 mL deionized water in the presence of sodium dodecyl sulfate at 80 °C for 2 h. The unreacted monomer was removed with a rotary evaporator under a reduced pressure at 80 °C for 1 h. The total solid content and surfactant concentration were adjusted to 10 w/w% and 0.2 w/w%, respectively (Fig. 1).

Fig. 3 Latex-state ^{13}C -NMR spectra for PBA at 323, 333, 343, and 353 K**Fig. 4** Temperature dependence of the half width for PBA latex

Characterization

Solution-state and latex-state NMR spectra were measured with a JEOL JNM FT-NMR AL400 spectrometer operating at 399.7 and 100.4 MHz for ^1H and ^{13}C , respectively. For the solution-state NMR measurements, dried PBA was dissolved into chloroform- d (Nacalai Tesque) without tetramethylsilane (TMS), whereas PBA latex with deuterium oxide (Nacalai Tesque) was used without further treatment for the latex-state NMR measurements. The NMR measurements were performed at a pulse width of 30° (5 μsec) and pulse repetition time of 5.0 s, and a number of scans, thus applied, was 1000. Measurement of spin-spin relaxation time (T_2) was performed by pulse sequenced CPMG with pulse repetition time of 6.2 s at a pulse width of 90° (PW1) and 180° (PW2) and a relaxation delay of

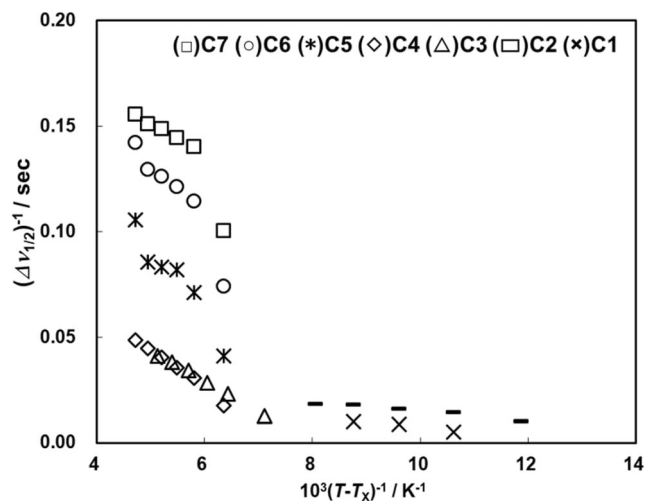


Fig. 5 Master curve of the half width superimposed with $(T-T_X)$ for PBA

5.000 s. The measurement was carried out by using 32,768 data point at 323–363 K. Differential scanning calorimetry (DSC) measurements were performed with an SII Nano Technology DSC7020 differential scanning calorimeter over a temperature range of -150 to 150 °C at the heating rate of 10 °C. The samples (~ 10 mg) were encapsulated in an aluminum pan. The glass transition temperature, T_g , of the sample was determined from the inflection point in the DSC curve. The particle size was measured with a Coulter LS230 Laser Diffraction particle size analyzer. PBA latex was dispersed in a sodium dodecyl sulfate solution (0.1 w/w%) to obtain latex samples with DRC ~ 3 w/w%.

Results and discussion

Figure 2a, b shows the ^{13}C -NMR spectra for PBA latex at 353 K in the latex-state and solution-state NMR spectra,

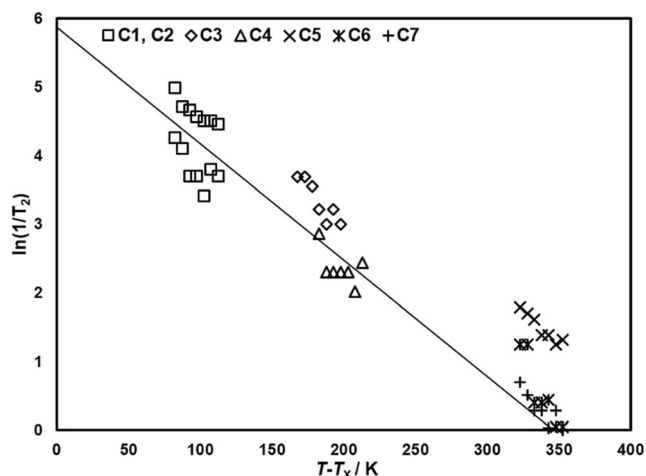


Fig. 6 Master curve of the half width superimposed with $T-T_X$ for PBA before determining T_X for C5, C6, and C7

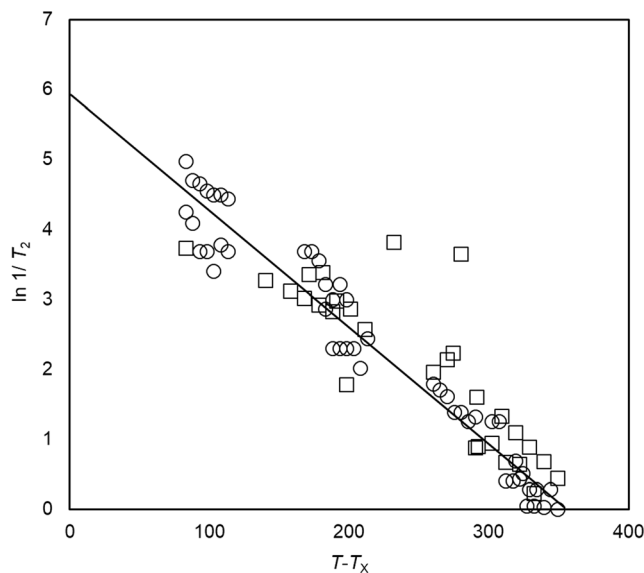


Fig. 7 Master curve of the half width superimposed with $T-T_X$ for PBA after determining the T_X for C5, C6, and C7

respectively. The ^{13}C -NMR spectrum for PBA has seven signals at 35, 41, 174, 64, 30, 19, and 14 ppm, which were previously assigned to C1, C2, C3, C4, C5, C6, and C7 of the butyl acrylate units [15–17]. The values of half width of the signals in the latex-state ^{13}C -NMR spectrum for PBA are similar to those in the solution-state ^{13}C -NMR spectrum (Table 1). The narrow half width of the signals in the latex-state ^{13}C -NMR spectrum for PBA may imply that a high resolution is achieved by not only the active motion of PBA but also by the rotational movement of the dispersoid since PBA in the dispersoid is in the solid state. Table 2 shows the value of the glass transition temperature, T_g , and the volume mean particle diameter for PBA.

To investigate the effect of active motion of PBA and the rotational movement of the dispersoid more precisely,

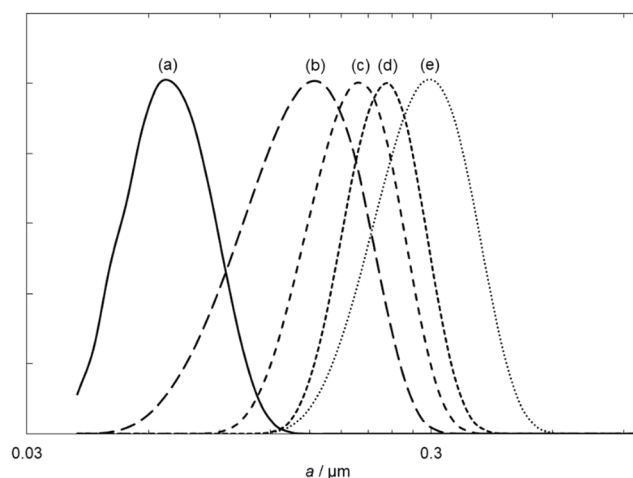


Fig. 8 Particle size distribution of PBA latex. Average particle size is (a) 78 nm, (b) 150 nm, (c) 212 nm, (d) 250 nm, and (e) 300 nm

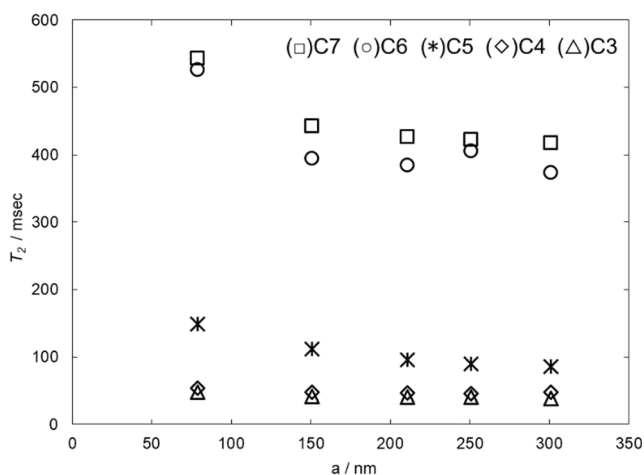


Fig. 9 T_2 versus the average particle size for PBA latex

we focused on the half width of PBA latex. Figure 3 shows the latex-state ^{13}C -NMR spectra for PBA at various temperatures (323, 333, 343, and 353 K). At 323 K, the signals of C1, C2, and C3 are very broad. This may be due to the reduced motions of PBA and the slow rotational movements of the dispersoid. These signals narrow as temperature increases. For example, the value of the half width of C7 decreases from 6 to 3 Hz as the temperature rises from 323 to 353 K. In addition, the value of the C3 signal decreases from 40 to 20 Hz. However, there is a difference in the absolute value of the half width between the C7 and C3; the value of the half width of C3 is much larger than that of C7.

Figure 4 shows the temperature dependence of the half width for PBA latex. A higher temperature results in a lower half width value. The value of the half width of the C7 signal is the lowest among the carbons, whereas that of the C1 is the highest. This may be due to the difference in the local molecular motion of PBA.

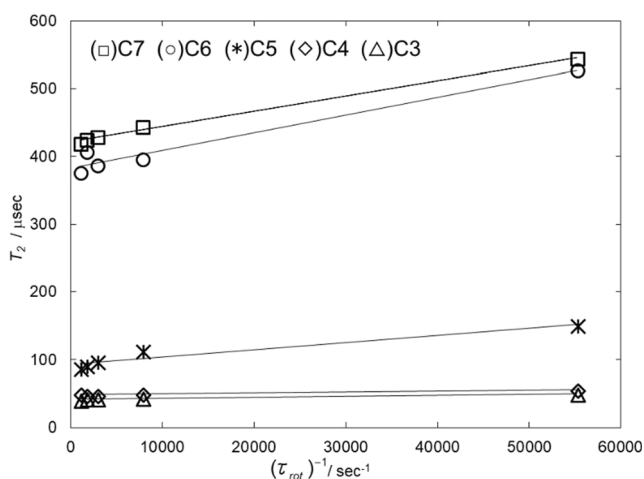


Fig. 10 T_2 versus reciprocal τ_{rot} for PBA latex

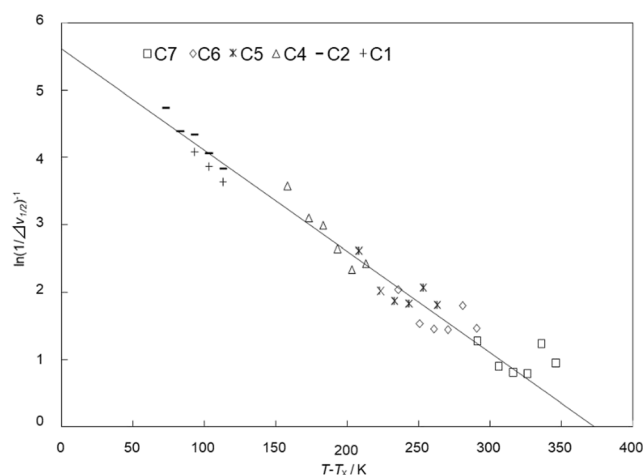


Fig. 11 Master curve of the half width superimposed with $T-T_X$ for PBA with a volume mean particle diameter of 300 nm

In the terms of the relationship between the relaxation time and the molecular motion, the spin-spin relaxation time, T_2 , depends on the correlation time of the motion. Therefore, the difference in T_2 may originate from the difference in local molecular motions. In other words, the difference in the half width may reflect a change in the local molecular motion. The local molecular motion is usually associated with the relaxation temperatures, which are determined by dielectric constant measurements. For instance, the α relaxation is related to the micro-Brownian motion of the main chain, β -relaxation is related to the local bending motion of the main chain, and γ -relaxation is related to the motion of the pendant group. Figure 5 plots the reciprocal half width versus reciprocal $(T-T_X)^{-1}$, where T_X is the characteristic temperature. According to the literature, $T_\alpha = 240$ K, $T_\beta = 155$ K, and $T_\gamma = 142$ K. The values of the half width of the C1, C2, C3, and C4 signals are well superimposed by T_α , T_β , and T_γ , whereas those of C5, C6, and C7 are not. This may be due to the incorrect selection of T_X for C5, C6, and C7. Therefore, we assumed $T_X = 0$ K for C6 and C7 signals and removed the data for C5 to obtain the master curve for the reciprocal half width versus reciprocal $(T-T_X)^{-1}$. However, we are concerned about the ambiguity of the fitting procedure.

Table 3 Determined reference temperature, T_X

	PBA 70 nm	PBA 300 nm
C7	27.2	7.1
C6	64.4	62.5
C5	91.3	89.7
C4	140	140
C3	157	157
C2	240	240
C1	240	240

We reconsidered the relationship between T_2 and the molecular motion since a linear relationship could not be obtained in a semi-logarithmic plot of T_2 versus reciprocal ($T-T_X$). We assumed that T_2 is related to the molecular motion, where the molecular motion is proportional to $(T-T_X)$. Figure 6 plots the half width of the latex-state ^{13}C -NMR spectra for PBA latex versus $(T-T_X)$. Using the literature values of T_α , T_β , and T_γ for C1, C2, C3, and C4, the reciprocal half width is proportional to $(T-T_X)$. However, the reciprocal half widths for C5, C6, and C7 deviate from the linear regression line. Therefore, we tried to use T_X as the fitting parameter. T_X for C5, C6, and C7 were determined by superimposing the half width against the temperature.

Figure 7 plots the master curve of the half width and T_2 versus $T-T_X$ for PBA after determining T_X for the C5, C6, and C7 signals. The values are $T_\delta = 63$ K for C5, $T_\epsilon = 21$ K for C6 and $T_\zeta = 4$ K for C7. In the previous work, the motion of the pendant group is regarded as one relaxation mode. However, in the present work, we successfully analyzed various relaxation modes. We believe that this is an advantage of latex-state NMR spectroscopy.

Figure 8 shows the particle size distribution of PBA latexes with an average particle size of (a) 78 nm, (b) 150 nm, (c) 210 nm, (d) 250 nm, and (e) 300 nm. Each latex provides a uniform symmetrical distribution.

Figure 9 shows the T_2 versus the volume mean particle diameter for PBA latexes. The smaller the dispersoid, the longer the spin-spin relaxation time. This implies that latex with a smaller dispersoid provides a higher resolution NMR spectrum. The rotational movement of the dispersoid is expressed as Eq. (1).

$$(\tau_{rot})^{-1} = \frac{3TK_B}{4\pi\eta a^3} \quad (1)$$

where, k_B , Boltzmann constant; π , circular constant; η , viscosity of water; and a , particle radius.

Figure 10 plots T_2 versus reciprocal, τ_{rot} , for PBA latex. T_2 is linearly proportional to τ_{rot} . The higher the τ_{rot} value, the longer T_2 , confirming that T_2 depends upon the rotational movement of the dispersoid. The dependence is much stronger for C7 and C6, which are the terminal units of the pendant group.

Figure 11 plots the half width of the latex-state ^{13}C -NMR spectra for PBA latex versus $T-T_X$. Latex with a volume mean particle diameter of 300 nm yields a similar linear line. Table 3 summarizes the determined values at the reference temperature, T_X . Both the volume mean particle diameters give similar results, demonstrating that the molecular motions of the polymer are independent of the particle size, although the absolute values of the half width depend on the particle size. This is strong evidence that latex-state NMR spectroscopy effectively investigates the local molecular motions of vinyl polymers.

Conclusion

The half width depends upon the temperature and the particle size. The half width and the spin-spin relaxation time, T_2 , for PBA are superimposed onto the master curve with the reference temperature, T_X , which is independent of the particle size. The resolution and relaxation time of the latex-state ^{13}C -NMR spectrum for PBA are associated with the local motions of the polymer in the dispersoid. This study demonstrates that latex-state NMR spectroscopy is a powerful technique to investigate the molecular motions of a polymer.

Funding information This work was supported in part by a Grant-in-Aid (16H02291) for Scientific Research (A) from the Japan Society for the Promotion of Science.

Compliance with ethical standards

This work complies with ethical standards.

Conflict of interest The authors declare that they have no conflict of interest.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

References

- Ribelles JLG, Duenas JMM, Pradas MM (1989) Dielectric relaxation in poly(methyl acrylate), poly(ethyl acrylate), and poly(butyl acrylate). *J Appl Polym Sci* 38:1145–1157. <https://doi.org/10.1002/app.1989.070380612>
- Gaborieau M, Graf R, Kahe S, Pakula T, Spiess HW (2007) Chain dynamics in poly(*n*-alkyl acrylates) by solid-state NMR, dielectric, and mechanical spectroscopies. *Macromolecules* 40:6249–6256. <https://doi.org/10.1021/ma0706531>
- Dejean de la Batie R, Laupretre F, Monnerie L (1988) Carbon-13 NMR investigation of local dynamics in bulk polymers at temperatures above the glass transition temperature. 1. Poly(vinyl methyl ether). *Macromolecules* 21:2045–2052. <https://doi.org/10.1021/ma00185a028>
- Kikuchi H, Tokumitsu H, Seki K (1993) Molecular motions of poly(ethyl acrylate) and poly(*n*-butyl acrylate) studies by solid-state NMR and molecular dynamics computer experiments. *Macromolecules* 26:7326–7332. <https://doi.org/10.1021/ma00078a032>
- Kawahara S, Bushimata S, Sugiyama T, Hashimoto C, Tanaka Y (1999) A novel method for ^{13}C -NMR spectroscopy of polymer in emulsion: quantitative analysis of microstructure of crosslinked polybutadiene in latex. *Rubber Chem Technol* 72:844–853. <https://doi.org/10.5254/1.3538836>
- Kawahara S, Washio K, Morita T, Tanaka Y, Isono Y (2001) High-resolution latex-state ^{13}C -NMR spectroscopy: Part II Effect of particle size and temperature. *Rubber Chem Technol* 74:295–302. <https://doi.org/10.5254/1.3544951>
- Munie GC, Jonas J, Rowland TJ (1980) NMR relaxation study of crosslinked *cis*-1,4-polybutadiene. *J Polymer Sci, ChemEd* 18: 1061–1070. <https://doi.org/10.1002/pol.1980.170180324>
- Folland R, Steven JH, Charlesby A (1978) Proton spin relaxation in liquid polydimethylsiloxane: molecular motion and network

- formation. *J Polym Sci Phys Ed* 16:1041–1057. <https://doi.org/10.1002/pol.1978.180160611>
9. Folland R, Charlesby A (1979) Pulsed n. m. r. of *cis*-polyisoprene: 1. *Polymer* 20:207–210. [https://doi.org/10.1016/0032-3861\(79\)90223-4](https://doi.org/10.1016/0032-3861(79)90223-4)
 10. Folland R, Charlesby A (1979) Pulsed n. m. r. of *cis*-polyisoprene: 2. *Polymer* 20:211–214. [https://doi.org/10.1016/0032-3861\(79\)90224-6](https://doi.org/10.1016/0032-3861(79)90224-6)
 11. Ukawa J, Kawahara S, Sakai J (2007) Structural characterization of vulcanized natural rubber by latex-state ^{13}C NMR spectroscopy. *J Polym Sci: Part B: Polym Physics* 45:1003–1009. <https://doi.org/10.1002/polb.21076>
 12. Kwahara S (2011) Latex-state and solid-state NMR spectroscopy of elastomers, in ACS symposium series, 1077 (NMR Spectroscopy of Polymers), pp. 475–494. <https://doi.org/10.1021/bk-2011-1077.ch029>
 13. Sea-heng K et al (2017) Latex-state NMR spectroscopy for quantitative analysis of epoxidized deprotenized natural rubber. *Polym Adv Technol* 28:1156–1161. <https://doi.org/10.1002/pat.4008>
 14. Fukuhara L et al (2015) Study on the resolution of latex-state NMR spectroscopy. *Kobunshi Ronbunshu* 72:22–30. <https://doi.org/10.1295/koron.2014-0066>
 15. Lovell PA, Shah TH, Heatley F (1991) Chain transfer to polymer in emulsion polymerization of n-butyl acrylate studied by carbon-13 NMR spectroscopy and gel permeation chromatography. *Polymer communications*, 32, 98–103
 16. Kawamura T, Toshima N, Matsuzaki K (1995) Assignment of finely resolved ^{13}C -NMR spectra of polyacrylates. *Macromol Chem Phys* 196:3415–3424. <https://doi.org/10.1002/macp.1995.021961026>
 17. Pichot C, Llauro MF, Pham QT (1981) Microstructure of vinyl acetate-butyl acrylate copolymers studied by ^{13}C -NMR spectroscopy: influence of emulsion polymerization process. *J Polym Sci Part A Polym Chem* 19:2619–2633. <https://doi.org/10.1002/pol.1981.170191021>