^{13}C n.m.r. study of the microstructure of polynorbornadiene

Akira Mizuno*, Mitsuhiko Onda* and Toshihiro Sagane†
** Materials Science and Analysis Laboratories and † Iwakuni Polymer Research Laboratories, Mitsui Petrochemical Industries Ltd, Waki-cho, Kuga-gun, Yamaguchi-ken 740, Japan*

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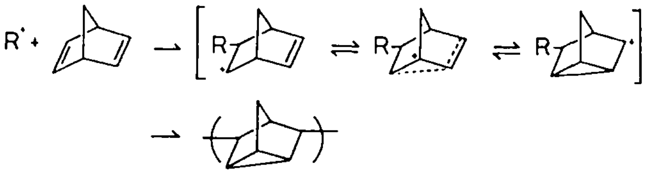
Polynorbornadiene obtained with an $AlEtCl_2$/t-BuCl catalyst system at −50°C was successively fractionated by boiling toluene and *o*-dichlorobenzene, with the result that the boiling toluene soluble portion was the major fraction. The microstructures of both the toluene soluble and *o*-dichlorobenzene insoluble fractions were characterized by high resolution ^{13}C nuclear magnetic resonance spectroscopy in solution and/or in the solid state and by differential scanning calorimetry. Both polymer fractions were shown to contain the repeating 3,5-disubstituted nortricyclene unit with exo/exo and exo/endo placements present in a 55:45 ratio. The polymerization mechanism involving the stereoregular addition of a norbornadiene monomer to the carbonium ion at the growing polymer chain-end was also proposed.

(Keywords: stereostructure; polynorbornadiene; $AlEtCl_2$/t-BuCl; 3,5-disubstituted nortricyclene; ^{13}C n.m.r.)

INTRODUCTION

The cationic polymerization of norbornadiene (NBD) by $AlCl_3$ catalyst in ethyl chloride and/or methylene chloride at temperatures from +40 to −123°C was first investigated by Kennedy and Hinlicky more than 20 years ago[1]. They found that the polymer (PNBD) obtained at the lowest temperature (−123°C) was completely soluble. Spectroscopic analysis by infra-red (i.r.) and ^{1}H nuclear magnetic resonance (n.m.r.) of the soluble polymer indicated that it has a regular 3,5-disubstituted nortricyclene structure. From this analysis, they proposed the following polymerization mechanism involving a transannular rearrangement:



PNBD is of great interest because it shows probably the highest glass transition temperature (T_g) of 320°C among linear, soluble and fusible addition-type hydrocarbon polymers so far[2].

In the present study, we prepared PNBD by cationic polymerization with $AlEtCl_2$/t-BuCl and studied its structure with the aid of high-field ^{13}C n.m.r. On the basis of detailed n.m.r. information on the polymer stereostructure, the polymerization mechanism concerning the stereoregular addition of a NBD monomer to the carbonium ion at the growing polymer chain-end was proposed.

EXPERIMENTAL

Polymerization of NBD

Cationic polymerization of NBD was carried out in CH_2Cl_2 at −50°C by an $AlEtCl_2$/t-BuCl catalyst system under a dry nitrogen atmosphere. The reaction conditions were as follows: $[NBD]_0$ 1.0 M, $[AlEtCl_2]_0$ 10.0 mM, $[t\text{-}BuCl]_0$ 5.0 mM, reaction time 60 min, reaction scale 200 ml.

For the polymerization reaction, t-BuCl solution in CH_2Cl_2 was added to the monomer solution, and $AlEtCl_2$ solution in n-hexane was then added to this mixture to initiate polymerization. The reaction was terminated with cold ammoniacal methanol. The quenched polymerization mixture was washed with water to remove the catalyst residue, and the product was recovered from the organic layer by prrecipitation into methanol and was dried in vacuum. The polymer (11.2 g, monomer conversion = 61%) was obtained as a white powder.

Fractionation of the polymer

According to *Scheme 1*, the pulverized polymer was fractionated into soluble and insoluble fractions using toluene and *o*-dichlorobenzene as solvents in a Soxhlet-type extractor.

The fraction soluble in boiling toluene, designated as PNBD-S, was recovered by evaporation of the solvent, and the fraction insoluble in boiling toluene and *o*-dichlorobenzene, PNBD-I, was recovered by filtration. Both fractions were dried in vacuum before analysis.

Synthesis of 3-ethylnortricyclene

3-Ethylnortricyclene, which was used as a model compound for the n.m.r. structural analysis of PNBD, was synthesized by the method reported previously[3].

N.m.r. analysis

The n.m.r. sample was prepared by dissolving ~80 mg of PNBD-S at 120°C in ~0.5 ml of *o*-dichlorobenzene, including ~0.05 ml of deuteriobenzene which was used for field stabilization, in a 5 mm o.d. glass tube.

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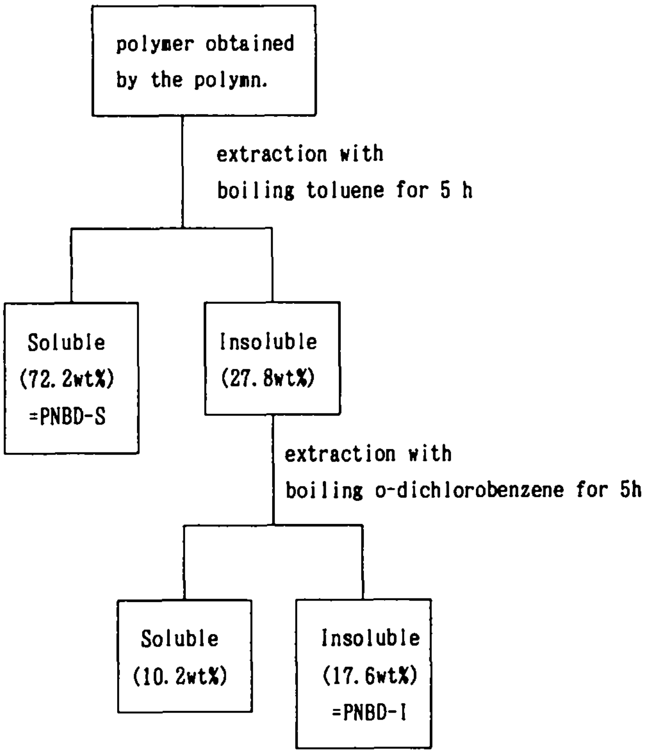


Scheme 1

The $^{13}C\{^1H\}$ n.m.r. spectrum was recorded on a Jeol GX-500 spectrometer operating at 125.8 MHz in a Fourier-transform mode. The instrumental conditions were as follows: pulse angle 45°; pulse repetition time 5.0 s; spectral width 20000 Hz; number of scans 10000; data point 64k. The ^1H decoupled ^{13}C distortionless enhancement through polarization transfer (d.e.p.t.) method was also used to discriminate the methylene peaks from the methine peaks. The ^{13}C n.m.r. spectrum of PNBD dissolved in deuteriochloroform at 50°C was also measured in order to observe olefinic carbon resonances, which may be hidden under the solvent resonance in the spectrum measured in *o*-dichlorobenzene.

The $^{13}C\{^1H\}$ spectrum of 3-ethylnortricyclene dissolved in deuteriochloroform in a 5 mm o.d. glass tube was observed at room temperature on the same spectrometer. The ^1H decoupled d.e.p.t. and heteronuclear C–H shift correlation 2D n.m.r. spectra were also measured in order to completely assign all the carbon peaks. The chemical shift data were used to estimate the γ-shift in the nortricyclene system.

^{13}C CP/MAS n.m.r. spectra for both PNBD-S and PNBD-I were measured at room temperature on a Jeol GSH-270 spectrometer operating at 67.8 MHz. The instrumental conditions were as follows: number of scans 8000; magic-angle spinning frequency 6 kHz; contact time 2 ms; decoupling field strength 60 kHz; pulse repetition time 5 s; data point 8k.

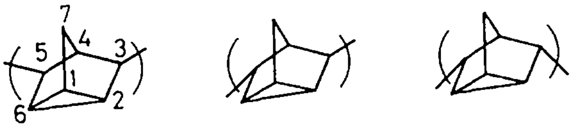
D.s.c. analysis

D.s.c. curves were recorded at a heating rate of 10°C min^{-1} in order to measure T_g for both PNBD-S and PNBD-I on a Seiko DSC 210 differential scanning calorimeter. The instrument was calibrated by measuring the melting points of indium and lead. The weight of the sample was ~5 mg.

RESULTS AND DISCUSSION

Preliminary n.m.r. analysis of PNBD-S

The ^{13}C n.m.r. spectrum of PNBD-S observed at 125.8 MHz in *o*-dichlorobenzene is shown in *Figure 1*. Carbon species of each peak were determined by d.e.p.t. measurement. Some methine peaks appeared at higher field (9 ~ 18 ppm) strongly indicating the existence of a three-membered ring. The olefinic carbon resonances with notable intensity were not observed in *o*-dichlorobenzene or deuteriochloroform solutions (spectrum not shown). By taking these results into account together with the ratio of total methylene to methine peak intensities (1/6), it is concluded that the nortricyclene unit has exclusively formed in the polymerization as Kennedy and Hinlicky proposed[1]. It is noticeable that there are two peaks which are assigned to the methylene resonances. The appearance of two methylene peaks in the ^{13}C n.m.r. spectrum might reflect the difference in placements of substituents at positions C_3 and C_5 across the nortricyclene ring, i.e. exo and endo placements, as follows:



(exo/exo) (endo/exo) (endo/endo)

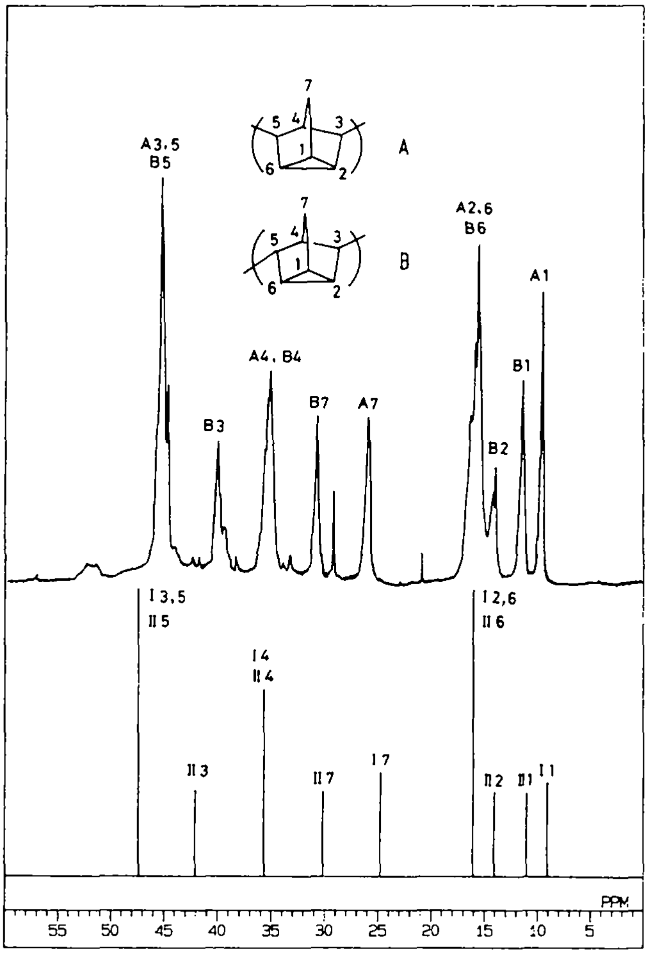


Figure 1 The 125 MHz ^{13}C n.m.r. spectrum of PNMD-S observed in *o*-dichlorobenzene at 120°C and the stick spectrum calculated based on the chemical shifts of model compounds I and II

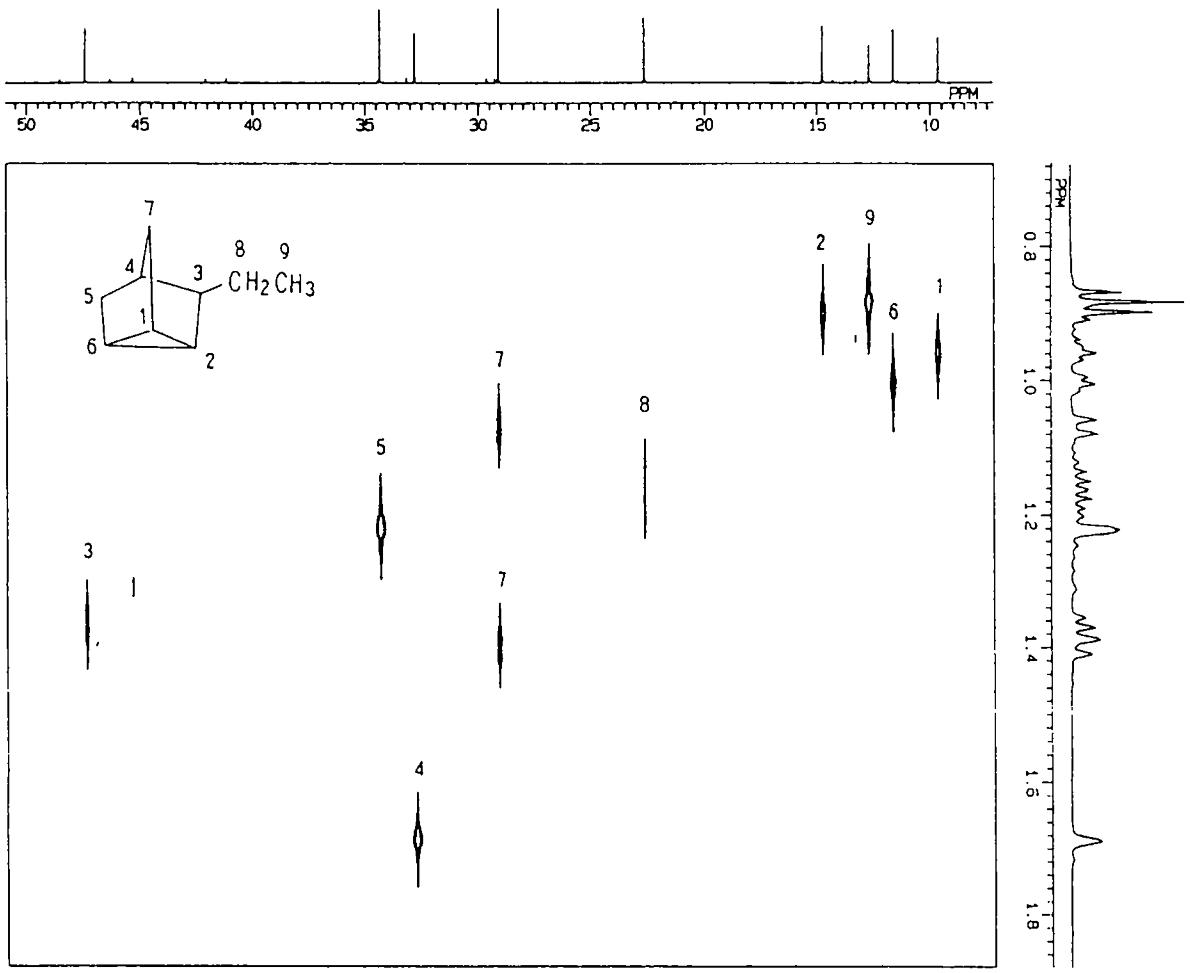


Figure 2 Heteronuclear C–H shift correlation 2D n.m.r. spectrum of 3-ethylnortricyclene in $CDCl_3$

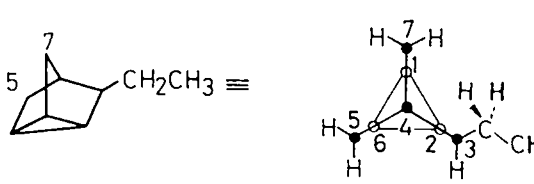
The exo/endo placements were analysed on the basis of the ^{13}C n.m.r. spectrum of the model compound as described below.

N.m.r. analysis of the model compound

3-Ethylnortricyclene was synthesized and its ^{13}C n.m.r. spectrum was fully analysed using ^1H decoupled d.e.p.t. and heteronuclear C–H shift correlation 2D n.m.r. spectra. The 2D C–H correlation spectrum is shown in *Figure 2*. In the analysis of the 2D n.m.r. spectrum, attention was focused on the assignments of the C5 and C7 resonances because the chemical shift difference between these two carbon resonances corresponds to the γ-shift in the nortricyclene system.

The γ-shift, which is the ^{13}C shift sterically induced by three-bond interaction[4], is useful for analysing the steric structures of hydrocarbons.

According to the following steric representation of 3-ethylnortricyclene:



the two protons bonded to the C7 atom must be magnetically non-equivalent because one of the protons is more affected by the through-space effect of the neighbouring ethyl group than the other which leads to a difference in chemical shift between them. Two protons bonded to the C5 atom resonate at nearly the same position due to the negligibly small difference in influence from the ethyl group. From this analysis, the methylene peaks resonating at 29.12 and 34.12 ppm in the ^{13}C n.m.r. spectrum are assigned to the C7 and C5 nuclei, respectively. Since the C7 and C5 atoms are in the *γ-gauche* and *γ-trans* positions with respect to the methylene carbon of the ethyl group, respectively, the γ-shift is estimated to be ~5 ppm in the nortricyclene system.

Garratt *et al.*[5] have extensively studied the structures of nortricyclenes having polar substituents by using X-ray and n.m.r. analysis. They pointed out that the γ-shift is not safely applied to the stereostructural analysis of nortricyclenes. However, the data presented here clearly show that the γ-shift may be safely applied to the stereostructural analysis of nortricycles as long as the substituents are non-polar.

The other carbon peaks were assigned on the basis of 2D n.m.r. analysis and with the aid of assignments of related compounds found in the literature[6,7]. The results are shown in *Figure 2* and are summarized in *Table 1*.

A comparison of the ^{13}C n.m.r. spectral data of nortricyclene by Della and Pigou[6] and our present data enables us to estimate the chemical shift changes of ring carbons induced by ethyl substituents (*Table 1*). These are then utilized to calculate the chemical shifts of the

Table 1 ^{13}C chemical shifts of 3-ethylnortricyclene[a]

Peak no.	Carbon species	Chemical shifts (ppm)	Shift difference from nortricyclene (ppm)
C1	CH	9.67	−0.63
C2	CH	14.75	+4.45
C3	CH	47.42	+14.02
C4	CH	32.83	+2.93
C5	CH_2	34.36	+0.96
C6	CH	11.64	+1.34
C7	CH_2	29.12	−4.28
C8	CH_2	22.67	-
C9	CH_3	14.75	-

[a] Numbering of carbon atoms is as follows:

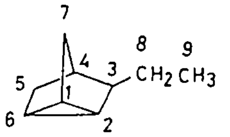
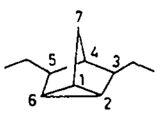


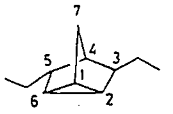
Table 2 Calculated ^{13}C chemical shifts of three 3,5-diethylnortricyclene isomers[a]

Peak no.	Carbon species	Chemical shifts (ppm) I	II	III	Polymer (obs.)
C1	CH	9.04	11.01	12.98	9.9, 11.8
C2	CH	16.09	14.12	14.12	15.7, 14.1
C3	CH	48.38	43.14	43.14	45.6, 40.1
C4	CH	35.76	35.76	35.76	35.4
C5	CH	48.38	48.38	43.14	45.6
C6	CH	16.09	16.09	14.12	15.7
C7	CH_2	24.84	30.08	35.32	26.2, 31.0

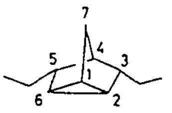
[a] I



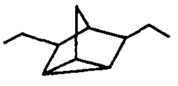
II



III



three 3,5-diethylnortricyclene isomers shown below, on the assumption that substituent contributions are additive:



I
(exo/exo)

II
(endo/exo)

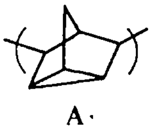
III
(endo/endo)

The calculated chemical shift data are listed in *Table 2*. These data were used to analyse the stereochemical structure of PNBD.

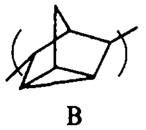
N.m.r. analysis of the stereochemical structure of PNBD-S

Since the methylene resonance of PNBD was unambiguously assigned to C7 in the nortricyclene skeleton, attention was focused on the two methylene peaks of PNBD-S resonating at 26.2 and 31.0 ppm in the ^{13}C n.m.r. spectrum in *Figure 1*. The chemical shifts of these two methylene peaks were in good agreement with those of the corresponding carbon nuclei of model compounds I and II shown in *Table 2*. The other carbon peaks of the polymer were also assigned with the aid of ^{13}C shifts of these model compounds.

Figure 1 shows a stick spectrum predicted on the basis of chemical shifts of the model compounds in comparison with the observed spectrum. The predicted stick spectrum fits nicely with the observed one except for the C3 and C5 resonances, the chemical shifts of which are more influenced by substituent species due to direct bonding. From these results, it is concluded that PNBD-S is constructed from two types of repeating units as shown below:



A·
(exo/exo)



B
(endo/exo)

The ratio of type A to type B is easily calculated by the peak area ratio $S_{9.9}/S_{11.8}$ or $S_{26.2}/S_{31.0}$, giving 55/45, where $S_{9.9}$ is, for instance, the area of the peak resonating at 9.9 ppm.

Comparison between structures of PNBD-S and PNBD-I by ^{13}C cross-polarization/magic angle spinning (CP/MAS) and T_g measurements

The ^{13}C CP/MAS n.m.r. spectra of both PNBD-S and PNBD-I are shown in *Figure 3*. Ordinarily, the crystalline part or the rigid part of the polymer is mainly observed in the CP/MAS measurement. The present measurements were performed at room temperature, which is much lower than the T_g of the PNBD polymers, resulting in complete structural information being obtained. As shown in *Figure 3*, there are no significant differences between these two spectra, indicating that the structure of PNBD-I is essentially the same as that of PNBD-S. Also, these two spectra are similar to that of

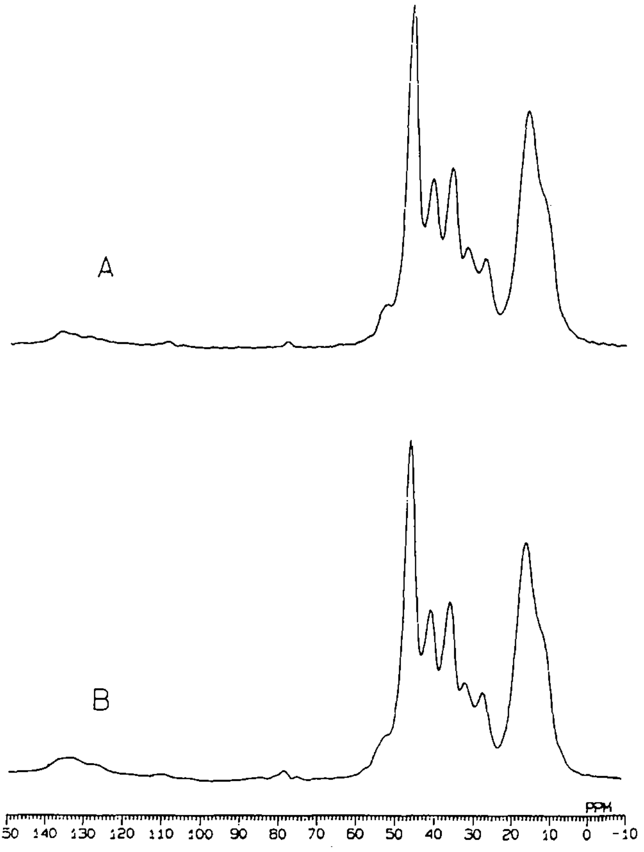
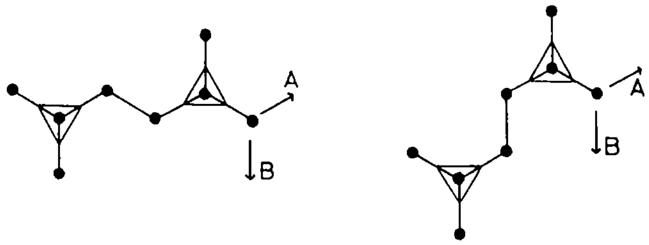
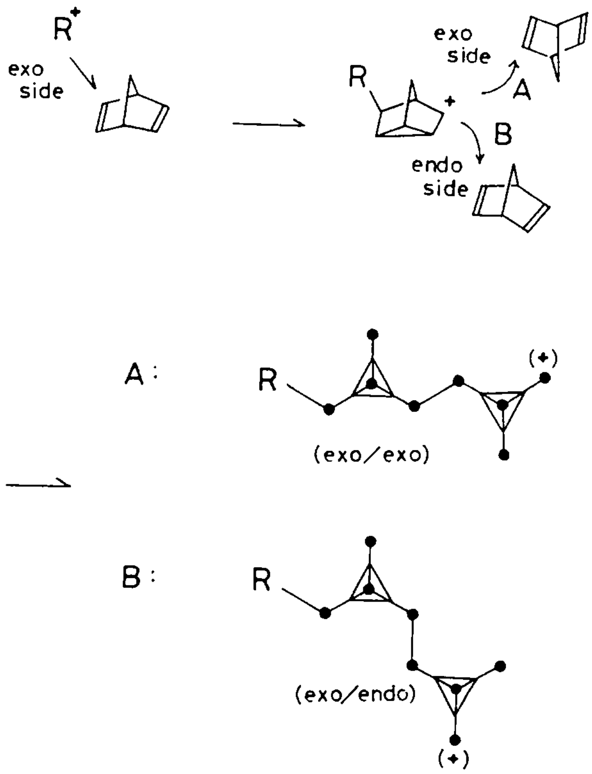


Figure 3 The ^{13}C CP/MAS n.m.r. spectra of PNBD-S(A) and PNBD-I(B)



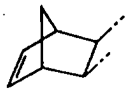
Scheme 2 Polymerization proceeds either in direction A or B (left) or only in direction A (right)



Scheme 3

PNBD-S observed in the liquid state (*Figure 1*), although the peaks are much broader in the ^{13}C CP/MAS n.m.r. spectrum owing to its inherent width.

Furthermore, each ^{13}C CP/MAS n.m.r. spectrum includes a small broad resonance in the olefinic carbon region of 125–140 ppm, suggesting that a 2,3-type reaction occurs, even though its frequency is very low, leading to crosslinking of the polymer.



2,3-type addition

However, no direct evidence of the crosslinked structure was obtained in our analysis probably due to its weak existence even in PNBD-I.

In addition, d.s.c. analysis was carried out for each fractionated polymer. PSBD-S and PSBD-I did not exhibit a large difference in T_gs, namely 290°C for PNBD-S and 283°C for PNBD-I. The results of the d.s.c. tests, although not conclusive with respect to chemical structure, support the ^{13}C CP/MAS n.m.r. analyses, indicating that both polymers have fundamentally the same structures.

Polymerization mechanism

The cationic polymerization of norbornadiene gives a polymer with two stereoisomeric 3,5-disubstituted nortricyclene repeat units, that is, exo/exo and exo/endo structures.

The reason why the endo/endo structure is not formed is probably due to the penultimate effect involving steric hindrance. The reaction mechanism proposed is shown in *Scheme 2*.

Alvernhe *et al.*[8] have extensively studied the bromofluorination of norbornadiene using *N*-bromosuccinoimide and $Et_3N/3HF$ which leads to a 3:2 mixture of 3-exo-bromo-5-exo-fluoronortricyclene and 3-exo-bromo-5-endo-fluoronortricyclene. They concluded that the bromonium species attack on the exo site of norbornadiene.

If this mechanism can be applied to the polymerization of norbornadiene, the carbonium ion on the growing polymer chain-end attacks norbornadiene from only the exo side of the monomer, and then the notricyclene carbonium ion formed can propagate either from the exo or endo side of the nortricyclene structure to the exo side of the next monomer as shown in *Scheme 3*. This might be another possible reason why any endo/endo structure is not formed in our cationic polymerization.

From the two proposed mechanisms shown in *Schemes 2* and *3*, the latter, involving the carbonium ion attacking the monomer from only the exo side, is difficult to interpret. Therefore, we propose *Scheme 2*, involving the penultimate effect owing to steric hindrance, as the probable polymerization mechanism.

ACKNOWLEDGEMENT

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