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Study on the geometric structure of poly[1-(trimethylsilyl)-1-propyne] by ^{13}C and ^{29}Si NMR spectroscopies

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Summary

The geometric structure of poly[1-(trimethylsilyl)-1-propyne] was investigated by ^{13}C and ^{29}Si NMR spectroscopies. According to ^{13}C NMR, the geometric structure varied with polymerization catalysts. $NbCl_5$ was inferred to produce more cis-rich polymer than $TaCl_5$. On the other hand, polymerization conditions such as solvent, temperature and cocatalyst hardly affected the geometric structure. The cis contents of polymers bearing bulkier substituents ($-SiMe_2-nC_6H_{13}$, $-SiMe_2-CH_2SiMe_3$) prepared with $TaCl_5$ were similar to that of poly(TMSP) with $TaCl_5$.

Introduction

Polyacetylenes, which have alternating double bonds along the main chain, are expected to show different properties depending on the geometric structure of the main chain. The geometric structures of polyacetylene,[1] poly(*tert*-butylacetylene)[2,3] and some other substituted polyacetylenes have been elucidated by NMR and IR. Further, the effects of catalysts and polymerization conditions on the geometric structure have been studied. However, for the disubstituted acetylene polymers, which have no hydrogen atom directly bonded to the main chain, the geometric structure is rather difficult to observe, and, to our knowledge, there were no such studies.

We have found that the solubility property of poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)], one of the disubstituted acetylenes, changes with polymerization catalysts.[4] We presumed that the solubility change was due to geometric structure of the main chain rather than molecular weight. To prove it, we have examined the geometric structure of poly(TMSP) by ^{13}C and ^{29}Si NMR spectroscopies.[5]

Apart from our research, Costa et al. have quite recently studied the solution and solid ^{13}C NMR of poly(TMSP).[6] They found some differences of

^{13}C NMR spectra with polymerization catalysts similarly to our observations. They were, however, unable to determine the proportion of cis and trans structures from the insufficiently resolved spectra. Herein we report on the geometric structure of poly(TMSP) studied by ^{13}C and ^{29}Si NMR, and discuss how catalysts, polymerization conditions and bulky substituents on the Si of monomer affect on the geometric structure of polymer.

Experimental

Materials

1-(Trimethylsilyl)-1-propyne (TMSP) and its homologues were offered by Shin-etsu Chemical Industries, and were distilled twice over CaH_2; purity > 99.8% [gas chromatography (GC)]. Vinyltrimethylsilane was distilled twice over CaH_2; purity > 99.5% (GC). $TaCl_5$, $NbCl_5$ (Aldrich), and Ph_3Bi (Tokyo Chemicals) were used as received.

Polymerization

Polymerizations were carried out under dry nitrogen according to the procedure described before;[4] $[M]_0 = 0.50$ M, [Cat] = [Cocat] = 20 mM. When it was necessary to decrease polymer molecular weight and, in turn, obtain well-resolved NMR spectra, vinyltrimethylsilane[7] was added as chain transfer agent to the polymerizing system. The polymer samples were obtained in 10 - 60% yields, whose weight-average molecular weights ($\bar{M}_w$'s) were 1×10^4 - 10×10^4 according to gel permeation chromatography (polystyrene standard).

NMR Measurement

^{13}C NMR spectra were measured in a mixture of toluene-d_8 and toluene (1:4) at 100 °C on JEOL GSX-270 and GS-400 spectrometers; sample concentrations 7 - 20 w/v %. Chemical shifts were referenced relative to the quarternary carbon of toluene-d_8 (137.5 ppm).

^{29}Si NMR measurements were performed in $CDCl_3$ at 30 °C on a Varian XL-300 spectrometer using gated proton decoupling without NOE [pulse width 6.7 µsec (30°), pulse delay 60 sec]. Chemical shifts were referenced relative to Me_4Si (0 ppm).

Results and discussion

Effect of polymerization catalysts

Figure 1 shows ^{13}C NMR spectra of the poly(TMSP)s obtained with $NbCl_5$ and $TaCl_5$. Obviously, all the signals of the four carbons split, each of which roughly consists of two peaks. Though the spectral patterns resembled those reported by Costa et al,[6] the better resolved spectra enabled us to estimate the relative peak areas. For the polymer with $NbCl_5$, the relative peak areas (fractions) of the low-field peaks in signals a, c, and d, and of the high-field peak in signal b were all within 60±8% (Table I). For the polymer with $TaCl_5$, on the other hand, the corresponding peak areas were within 38±8%. The splitting of these signals is probably attributable to the geometric structure of the main chain.

We have found that Mo-based catalysts produce all-cis or cis-rich poly(*tert*-butylacetylene)s, whereas W-based catalysts give non-stereospecific poly(*tert*-butylacetylene)s.[2] This is probably because Mo has a smaller radius of coordination sphere than W does. We have no information at the moment to assign each peak of poly(TMSP) to cis and trans structures. If one, however, postulates on the analogy of poly(*tert*-butylacetylene) that $NbCl_5$ produces a cis-rich poly(TMSP) as compared with $TaCl_5$, the cis contents of above stated $NbCl_5$- and $TaCl_5$-based polymers should be ca. 60% and 38%, respectively.

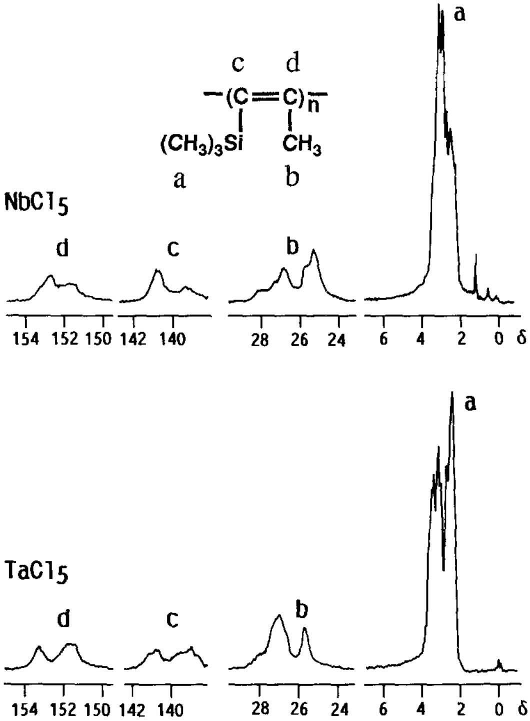


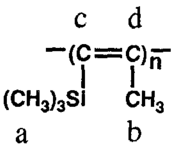
Figure 1. Effect of catalysts on the ^{13}C NMR spectra of poly(TMSP)s (polymerized at 80 °C for 24 h in toluene; $\bar{M}_w$ 3.6×10^4 ($NbCl_5$), 7.6×10^4 ($TaCl_5$); measured at 100 °C and 100 MHz for ^{13}C).

This difference in the geometric structure of poly(TMSP) is expected to bring about some differences in physical properties. In fact, poly(TMSP) obtained with $NbCl_5$ is less soluble than the one formed with $TaCl_5$ (e.g., the former is insoluble in *n*-hexane, whereas the latter is soluble), although the former polymer has a lower molecular weight. In this connection, it is noted that cis-rich poly(*tert*-butylacetylene)s produced with Mo-based catalysts are less soluble[2].

Table I

Relative peak area (%) of ^{13}C NMR of poly(TMSP)s [a, b]

catalyst	$f^a_{(L)}$	$f^b_{(H)}$	$f^c_{(L)}$	$f^d_{(L)}$
$NbCl_5$	60	55	68	53
$TaCl_5$	45	30	42	35



$$-(\underset{\underset{a}{(CH_3)_3Si}}{\overset{c}{C}}=\underset{\underset{b}{CH_3}}{\overset{d}{C}})_n-$$

a) $$f^a_{(L)}(\%) = \frac{\text{Area of the low-field peak of signal a}}{\text{Area of signal a}} \times 100,$$

and so on (subscripts L and H denote low- and high-field peaks, respectively).

b) See Figure 1 for polymerization conditions.

The ^{13}C NMR signal of Me_3Si group was rather complicated, and hence extended spectra are shown in Figure 2 (the left two spectra). Such complicated splittings should be due not only to the pertaining unit, but also to the neighboring few units. Thus the polymer with $NbCl_5$ exhibited a large peak at 2.9 ppm. In the polymer with $TaCl_5$, on the other hand, this peak was rather small, and large peaks were observed at 2.4 ppm and 3.4 ppm instead. This finding suggests that the polymer formed with $NbCl_5$ has a sequence distribution of geometric structure different from that with $TaCl_5$.

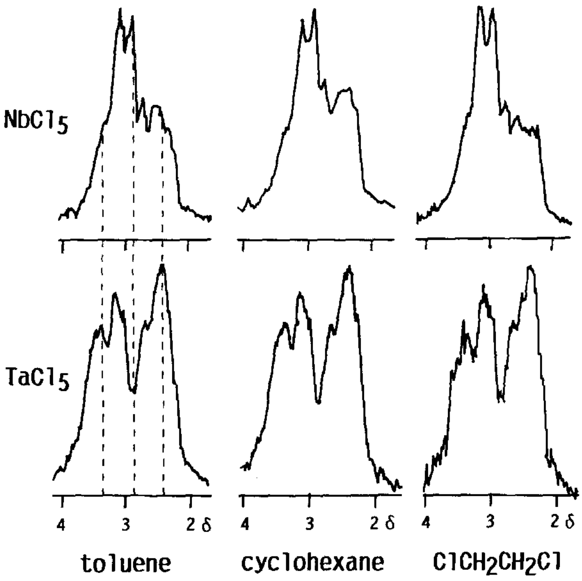


Figure 2. Effect of polymerization solvents on the Me_3Si region of ^{13}C NMR spectra of poly(TMSP)s (polymerized at 80 °C for 24 h; measured at 100 °C and 68 MHz for ^{13}C).

Figure 3 depicts ^{29}Si NMR spectra of the poly(TMSP)s prepared with $NbCl_5$ and $TaCl_5$. These spectra are fairly different from each other, as is the case of ^{13}C NMR. The spectrum of the polymer with $NbCl_5$ is composed of a single major peak centering at -9.9 ppm. The spectrum of the polymer with $TaCl_5$, in contrast, consists of three main peaks at -9.3, -9.9, and -10.8 ppm. Presumably, these ^{29}Si NMR spectra also should reflect the geometric structure of the polymer in a way slightly different from ^{13}C NMR spectra. The simpler spectral pattern of the $NbCl_5$-based polymer is probably due to a cis-rich structure and a longer sequence of geometric structures.

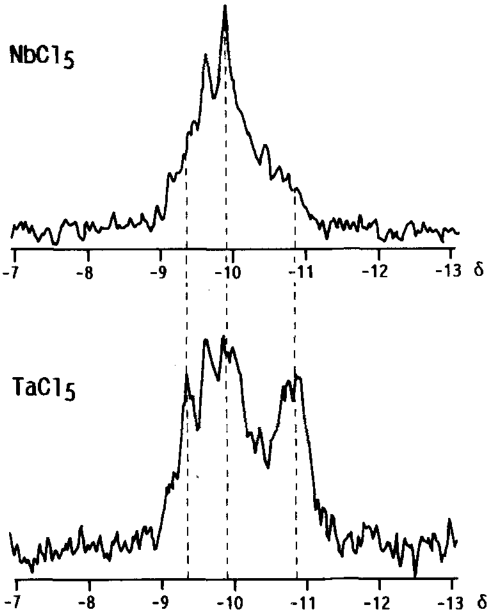


Figure 3. ^{29}Si NMR spectra of poly(TMSP)s (polymerized in toluene at 80 °C for 24 h; measured in $CDCl_3$ at 30 °C and 60 MHz for ^{29}Si).

Effect of polymerization conditions

Figure 2 illustrates the Me_3Si region of ^{13}C NMR spectra of the poly(TMSP)s obtained in several solvents. The signal patterns of the polymers formed in cyclohexane and 1,2-dichloroethane are virtually the same as those with toluene as polymerization solvent as far as the polymerization catalyst is the same. Further, the polymer obtained with $NbCl_5$ in anisole, an oxygen-containing solvent, also showed a spectrum very similar to the one with $NbCl_5$ in toluene ($TaCl_5$ afforded no polymer in anisole). Thus, the geometric structure of poly(TMSP) hardly depended on polymerization solvents. This result contrasts with the fact that the geometric structure of poly(*tert*-butylacetylene) is greatly affected by the kind of polymerization solvent.[2]

The effect of polymerization temperature was examined. The spectra of the polymers with $TaCl_5$ hardly changed over the temperature range, 30 - 100 °C. The spectra of the polymers produced with $NbCl_5$ in the range, 0 - 100

°C were also virtually identical to one another. Thus, the geometric structure of the polymer hardly varied within such temperature ranges that achieve high polymer yields.

It is known that use of Ph_3Bi as a cocatalyst appreciably accelerates TMSP polymerization and affords an extremely high molecular weight polymer.[8] The ^{13}C NMR spectra of the polymers obtained with $NbCl_5$-Ph_3Bi and $TaCl_5$-Ph_3Bi, however, were almost the same as those with $NbCl_5$ and $TaCl_5$ alone, respectively. Thus, the geometric structure of the polymer does not depend on the presence or absence of Ph_3Bi.

It is concluded from the above stated results that the geometric structure of poly(TMSP) is hardly affected by polymerization conditions unlike the kind of the central metal of the catalyst.

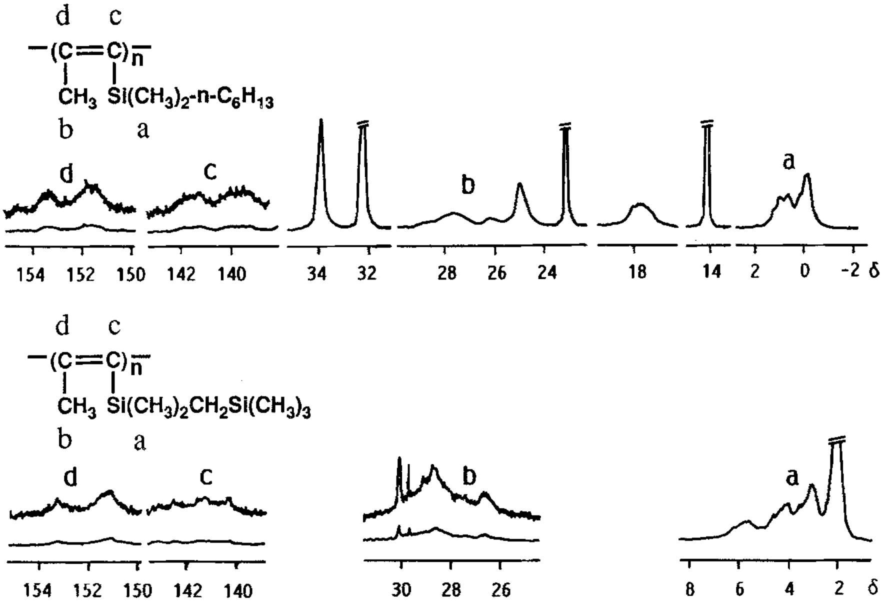


Figure 4. ^{13}C NMR spectra of poly(TMSP) homologues (polymerized in toluene at 80 °C by $TaCl_5$-Ph_3Bi (top) and $TaCl_5$ (bottom); measured at 100 °C and 100 MHz for ^{13}C).

Effect of the bulky substituents on Si

The ^{13}C NMR spectra of poly(TMSP) homologues[9,10] obtained with $TaCl_5$-based catalysts were examined (Figure 4; poly($MeC\equiv CSiMe_2R$), R = n-C_6H_{13}, CH_2SiMe_3). In both polymers, all of the four carbons corresponding to those of poly(TMSP) (i.e. Me_2Si, Me, and the two olefinic carbons) exhibit almost the same splitting patterns as those of $TaCl_5$-based poly(TMSP); their cis contents are both ca. 40%. Thus, the bulky substituents on Si hardly affect the geometric structure. The other carbons do not split probably because they are too distant from the main chain to reflect the geometric structure. It should be noted that $NbCl_5$-based catalysts afford polymers only in poor yields from these monomers owing to the steric hindrance of bulky substituents on Si.

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References

1. T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974).
2. Y. Okano, T. Masuda, and T. Higashimura, *Polym. J.*, **14**, 477 (1982).
3. T. J. Katz, T. H. Ho, N.-Y. Shih, Y.-C. Ying, and V. I. W. Stuart, *J. Am. Chem. Soc.*, **106**, 2659 (1984).
4. T. Masuda, E. Isobe, and T. Higashimura, *Macromolecules*, **18**, 841 (1985).
5. H. Izumikawa, T. Masuda, K. Tsuchihara, and T. Higashimura, *Polym. Prep. Jpn. (Engl. Ed.)*, **39**, E99 (1990).
6. G. Costa, A. Grosso, M. C. Sacchi, P. C. Stein, and L. Zetta, *Macromolecules*, **24**, 2858 (1991).
7. T. Masuda, H. Kouzai, and T. Higashimura, J. Chem. Soc., Chem. Commun., 252 (1991).
8. T. Masuda, E. Isobe, T. Hamano, and T. Higashimura, *Macromolecules*, **19**, 2448 (1986).
9. E. Isobe, T. Masuda, T. Higashimura, and A. Yamamoto, *J. Polym. Sci. Part A, Polym. Chem.*, **24**, 1839 (1986).
10. T. Masuda, E. Isobe, T. Hamano, and T. Higashimura, *J. Polym. Sci. Part A, Polym. Chem.*, **25**, 1353 (1987).

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