Metathesis copolymerization of norbornene with phenylacetylene and its ring-substituted derivatives catalysed by WCl_6: 2. Reactivity of monomers

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Effects of ring substituents of phenylacetylene (PA) were studied in the metathesis copolymerization of norbornene (NBE) with PA catalysed by WCl_6. The shape of copolymer composition curves indicated the formation of random copolymers in the copolymerizations of NBE with PA and its *para*- or *meta*-substituted derivatives. The more electron-withdrawing the substituent, the less reactive the PA; the Hammett plot of these systems gave a straight line with a negative slope ($\rho = -1.1$). In contrast, some composition curves for the copolymerizations of NBE with *ortho*-substituted PAs were sigmoidal. This difference is explained in terms of the steric hindrance of *ortho*-substituents, i.e. the propagation reaction between the *ortho*-substituted PA end and the NBE monomer seems sterically difficult.

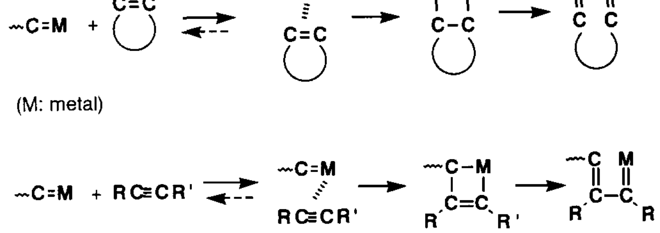
(Keywords: metathesis polymerization; copolymerization; norbornene; phenylacetylene; ring-substituted phenylacetylene; copolymer composition curve; monomer reactivity)

INTRODUCTION

In the preceding paper in this series[1] we reported copolymerization of bicyclo[2.2.1]hept-2-ene (norbornene; NBE), a strained cycloolefin, with phenylacetylene (PA) and its ring-substituted derivatives (PA(X)) catalysed by WCl_6, where copolymer formation was examined in detail. The NBE unit of the copolymerization products possessed the ring-opened structure formed by ring-opening metathesis polymerization (ROMP), and the NBE-PA(X) dyads were directly observed by H–H COSY n.m.r. spectroscopy. These findings demonstrate that the polymerization of substituted acetylenes by WCl_6 proceeds by the metathesis mechanism as well as ROMP of cycloolefins. Further, this copolymerization provides a method of synthesizing a novel type of copolymers.

There have been some studies on the copolymerization of substituted acetylenes by group 5 and 6 transition metal catalysts. In the copolymerization of PA with *para*-substituted phenylacetylenes, for example, a monomer with an electron-donating group exhibits a higher reactivity than that of PA[2]. This indicates that the active species of this polymerization possesses an electrophilic nature. Another tendency in the copolymerization of substituted acetylenes is that a sterically more hindered monomer is usually less reactive. For instance, the monomer reactivity in the copolymerization of PA with aliphatic mono-substituted acetylenes decreases in the following order; n-BuC≡CH > s-BuC≡CH > (PA) ≫ t-BuC≡CH[3]. These results lead to a conclusion that the relative reactivity of substituted acetylenes is governed by the coordinating ability of monomer to active species which is, in turn, determined by both electronic and steric factors.

It is now generally accepted that the propagation reaction of cycloolefin polymerization consists of reversible coordination of the monomer to a metal carbene, formation of a metallacyclobutane, and regeneration of a metal carbene by ring scission[4,5] (*Scheme 1*). Recent advances on living polymerization have further elucidated the reaction mechanism of ROMP[6,7]. A similar metal carbene mechanism seems to be valid also for the polymerization of substituted acetylenes[8]. Cycloolefins and substituted acetylenes, however, are quite different from each other in the structure and properties of monomer and propagating end. Hence it is interesting to study the polymerization behaviour and reactivity of substituted acetylenes in the copolymerization with cycloolefins.



Scheme 1

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In the present study, we examined the copolymerization of NBE with various ring-substituted phenylacetylene derivatives catalysed by WCl_6[9], focusing on the structure–reactivity relationship of phenylacetylenes. Phenylacetylenes with *para*- or *meta*-substituents formed random copolymers with NBE, and the relative reactivity of phenylacetylene derivatives can be explained simply in terms of the electronic effect of substituents. In contrast, the copolymerization of NBE with *ortho*-substituted phenylacetylenes yielded more or less blocky copolymers. The structure of propagating end is discussed on the basis of experimental results.

EXPERIMENTAL

Materials

PA and (*p*-methylphenyl) acetylene were commercially obtained, and [2,5-bis(trifluoromethyl)phenyl]acetylene [$(CF_3)_2PA$] and (*p*-butyl-*o,o,m,m*-tetrafluorophenyl)-acetylene (BuF_4PA) were offered by the Government Industrial Research Institute, Nagoya. Other phenylacetylenes were prepared from the corresponding iodobenzenes by the same method as in the preceding paper[1]. All these acetylene monomers were distilled twice from CaH_2 before use. NBE and toluene (polymerization solvent) were purified as described in the preceding paper[1]. WCl_6 (Furuuchi Chemicals, Japan; purity >99.9%) was commercially obtained and used without further purification.

Copolymerization and calculation of monomer reactivity ratios

Copolymerization reactions were initiated by adding a monomer solution to a WCl_6 solution (in toluene, 30°C, $[M]_{o,total} = 1.0$ M, $[WCl_6] = 5$–20 mM). Aliquots of the reaction solution were taken out at suitable time intervals, and poured into isobutyl alcohol to quench polymerization. The concentrations of residual monomers in each aliquot were determined by gas chromatography (g.c.).

As stated in the preceding paper[1], PA and some ring-substituted phenylacetylenes produce by-products such as cyclotrimer in their copolymerization with NBE. It turned out that the by-products formed only at an early stage of copolymerization. Thus it was impossible to determine the monomer reactivity ratios (MRRs) from analysis of the copolymerization products of low conversions. Hence, the change of monomer concentrations with time was monitored by g.c., and data were collected at middle stages where side reactions were negligible.

A detailed procedure of determining MRRs is as follows. Provided that the concentration of monomer M_i changes from $[M_i]_t$ to $[M_i]_{t'}$ between times t and t' ($t' > t > 0$; $i = 1, 2$), one can obtain an average mole fraction of M_1 in the copolymerization system (f_1) by the following equation:

$$f_1 = [M_1]_{av}/([M_1]_{av} + [M_2]_{av})$$

where $[M_i]_{av} = ([M_i]_t + [M_i]_{t'})/2$ ($i = 1$, 2). The mole fraction of M_1 unit in the copolymer formed (F_1) is given by:

$$F_1 = \Delta[M_1]/(\Delta[M_1] + \Delta[M_2])$$

where $\Delta[M_i] = [M_i]_t - [M_i]_{t'}$ ($i = 1$, 2). A time when oligomerization and cyclotrimerization had ceased was chosen as t, and the monomer conversions between t and t' were kept to about 15% in order to maintain the precision of g.c. Copolymerizations were carried out at several monomer feeds, and MRRs were calculated from nearly ten pairs of f_1 and F_1 by the method of Yezrielev *et al.*[10].

RESULTS AND DISCUSSION

Copolymerization of NBE with PA

Figure 1 shows the composition curve of the copolymerization of NBE with PA. The MRRs for this copolymerization were: $r_{NBE} = 0.22$, $r_{PA} = 4.8$, $r_{NBE} \times r_{PA} = 1.1$. These values indicate that PA is about five times as reactive as NBE irrespective of the kind of propagating ends, and that random copolymerization occurs between these different types of monomers.

Copolymerization of NBE with para- *or* meta-*substituted phenylacetylenes*

Copolymerizations of NBE with phenylacetylenes having *para*- or *meta*-substituents (CH_3, Cl and CF_3) were examined. *Figure 2* illustrates composition curves for the copolymerizations with *para*-substituted phenylacetylenes, and *Figure 3* shows those using *meta*-substituted phenylacetylenes. The MRRs of these copolymerizations are listed in *Table 1*. Both the symmetrical arc shapes of composition curves and the products of MRRs close to unity show that all these copolymerizations are random ones, in other words, the relative reactivity of monomers does not depend on the kind of propagating ends. This result is the same as for the copolymerization of NBE with PA. Regardless of *para*- or *meta*-isomers, the relative reactivity of these phenylacetylene derivatives to NBE decreased in the order, $CH_3 > (H) > Cl > CF_3$, i.e. with increasing electron-withdrawing effect of substituents. It is interesting to note that both *p*- and *m*-CF_3 substituted phenylacetylenes show reactivities fairly close to that of NBE.

The reciprocal r_{NBE} denotes the relative reactivity of a phenylacetylene derivative to NBE towards the NBE

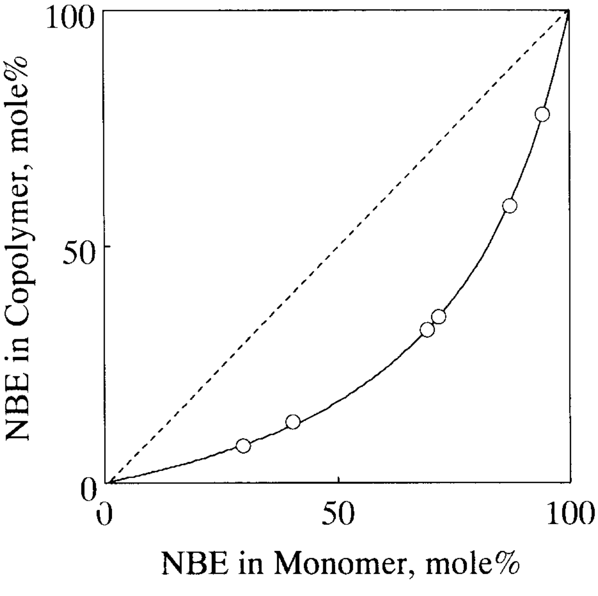


Figure 1 Composition curve for the copolymerization of NBE with PA (in toluene, 30°C, $[WCl_6] = 10$ mM, $[M]_{o,total} = 1.0$ M)

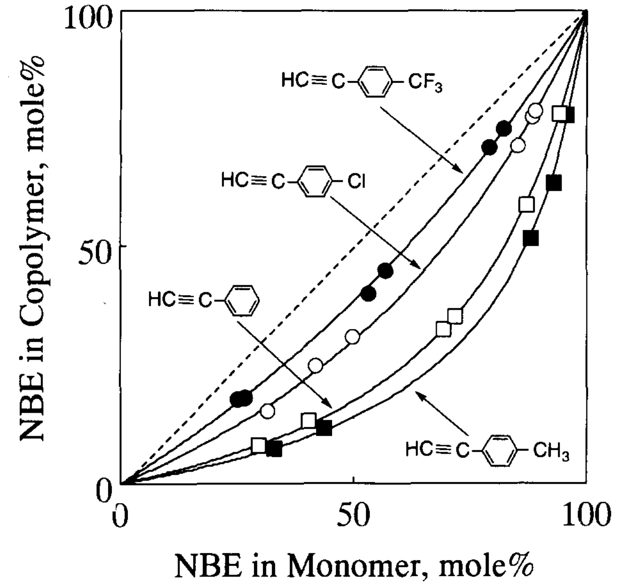


Figure 2 Composition curves for the copolymerizations of NBE with *para*-substituted phenylacetylenes (in toluene, 30°C, $[WCl_6] = 5\text{–}10$ mM, $[M]_{o,total} = 1.0$ M)

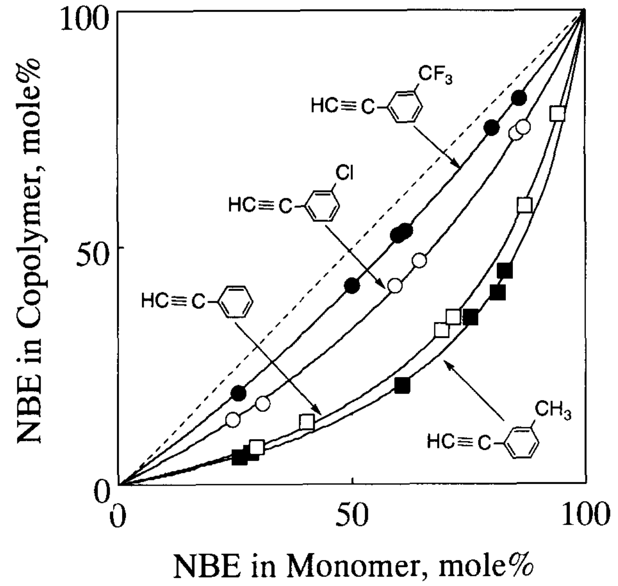


Figure 3 Composition curves for the copolymerizations of NBE with *meta*-substituted phenylacetylenes (in toluene, 30°C, $[WCl_6] = 5\text{–}10$ mM, $[M]_{o,total} = 1.0$ M)

propagating end for all these copolymerization systems. In *Figure 4* are plotted the $1/r_{NBE}$ values against the substituent constants (σ). This Hammett plot gives a good linear relationship, from the slope of which the reaction constant (ρ) is calculated to be -1.1. This negative ρ value means that the propagating end possesses an electrophilic nature, as was also observed in the copolymerization between phenylacetylenes[2].

Thus, PA and its *para*- or *meta*-isomers turned out to form random copolymers with NBE on the basis of the products of their MRRs. The relative reactivity of phenylacetylenes decreased by introduction of electron-withdrawing substituents.

Copolymerization of NBE with ortho-*substituted phenylacetylenes*

Figure 5 shows the composition curves of the copolymerizations of NBE with phenylacetylenes having *ortho*-substituents (CH_3, Cl and CF_3). The relative reactivity of these phenylacetylenes to NBE decreased qualitatively in the order, $CH_3 > (H) > Cl > CF_3$, as in the case of *para*- or *meta*-substituted phenylacetylenes. It is worth noting that the composition curves in *Figure 5* are more or less sigmoidal and accordingly the products of MRRs are larger than unity as shown in *Table 1*. This tendency of forming blocky copolymers is remarkable in the combination of NBE with [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3PA), for which the product of MRRs is as large as 13. In this copolymerization, both $r_{o\text{-}CF_3PA}$ and r_{NBE} are larger than unity (*Table 1*), which means that NBE is more reactive than *o*-CF_3PA

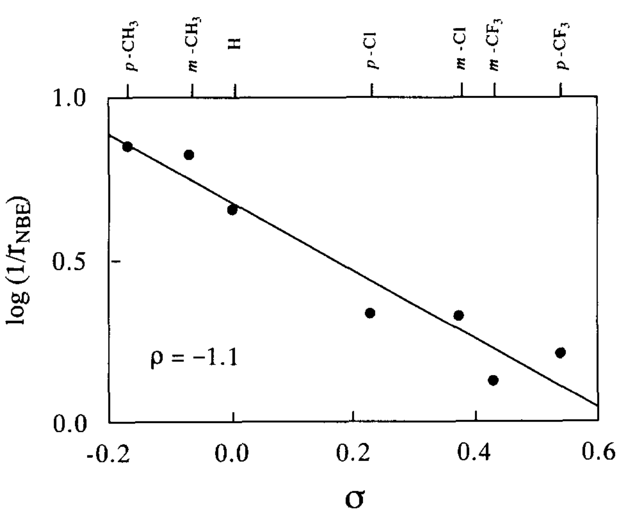


Figure 4 Hammett plot of $\log(1/r_{NBE})$ for the copolymerizations of NBE with *para*- and *meta*-substituted phenylacetylenes

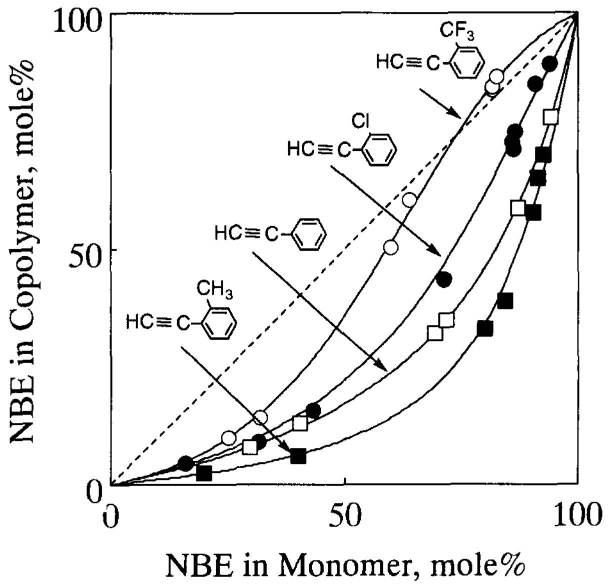


Figure 5 Composition curves for the copolymerizations of NBE with *ortho*-substituted phenylacetylenes (in toluene, 30°C, $[WCl_6] = 20$ mM, $[M]_{o,total} = 1.0$ M)

Table 1 Monomer reactivity ratios for the copolymerizations of NBE with ring-substituted phenylacetylenes (PA(X)) by WCl_6[a]

Substituent: X	$1/r_{NBE}$	$r_{PA(X)}$	$r_{NBE} \times r_{PA(X)}$
p-CH_3	7.1	6.1	0.82
m-CH_3	6.7	5.6	0.83
o-CH_3	4.6	10	2.3
H	4.6	4.8	1.1
p-Cl	2.2	2.4	1.1
m-Cl	2.1	2.0	0.96
o-Cl	1.6	4.6	2.9
p-CF_3	1.6	1.6	0.98
m-CF_3	1.3	1.4	1.1
o-CF_3	0.41	5.1	13
2,5-$(CF_3)_2$	0.06	1.9	30
p-Bu-*o*,*o*,*m*,*m*-F_4	0.19	0.32	1.7

[a] Polymerized in toluene at 30°C; $[WCl_6] = 5\text{–}20$ mM, $[M]_{o,total} = 1.0$ M

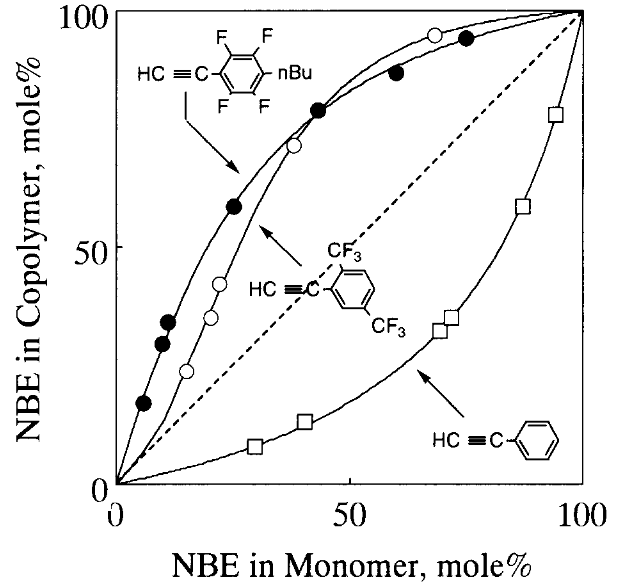


Figure 6 Composition curves for the copolymerizations of NBE with phenylacetylenes with many substituents (in toluene, 30°C, $[WCl_6] = 20$ mM, $[M]_{o,total} = 1.0$ M)

towards the NBE propagating end while the opposite is the case with the *o*-CF_3PA end.

In order to see how the steric effect of *ortho*-substituent affects the block character in copolymerization, two fluorine-containing phenylacetylenes, $(CF_3)_2$PA and BuF_4PA, were employed (*Figure 6*). These phenylacetylenes possess so many electron-withdrawing groups that, quite interestingly, they showed obviously smaller reactivities than NBE. Both the shapes of composition curves (*Figure 6*) and the products of MRRs (*Table 1*) indicate that the copolymerization using $(CF_3)_2$PA is blocky, while that using BuF_4PA is random. The molecular models drawn by computer graphics showed that $(CF_3)_2$PA is sterically much more crowded than BuF_4PA. Therefore the result obtained leads to a conclusion that the block character is caused by the steric hindrance of *ortho*-substituent and not by the electronic effect.

To corroborate further the generality of this block character in the copolymerization of NBE with sterically crowded, *ortho*-substituted phenylacetylenes, we studied the effect of trimethylsilyl group, a very bulky and rather electron-donating substituent (*Figure 7*). In the copolymerization of NBE with [*p*-(trimethylsilyl)phenyl]-acetylene (*p*-Me_3SiPA), both monomers were consumed simultaneously and the relative reactivity of both monomers does not appear to depend on conversion. On the other hand, [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA) showed much higher reactivity than that of NBE in the early stage of copolymerization. The consumption rate of NBE, however, gradually increased as the concentration of *o*-Me_3SiPA decreased with the progress of copolymerization. Thus, the relative reactivity of *o*-Me_3SiPA to NBE was as high as *ca* 40 in the period of time 10–30 min in *Figure 7*, but it decreased significantly to *ca* 4 in the period 30–115 min. This can be explained in terms of the idea that the relative consumption rate of NBE to *o*-Me_3SiPA increases as the *o*-Me_3SiPA propagating end decreases and the NBE end increases. Consequently this copolymerization should give a blocky copolymer.

All these findings indicate that phenylacetylenes with bulky *ortho*-substituents generally produce blocky copolymers with NBE.

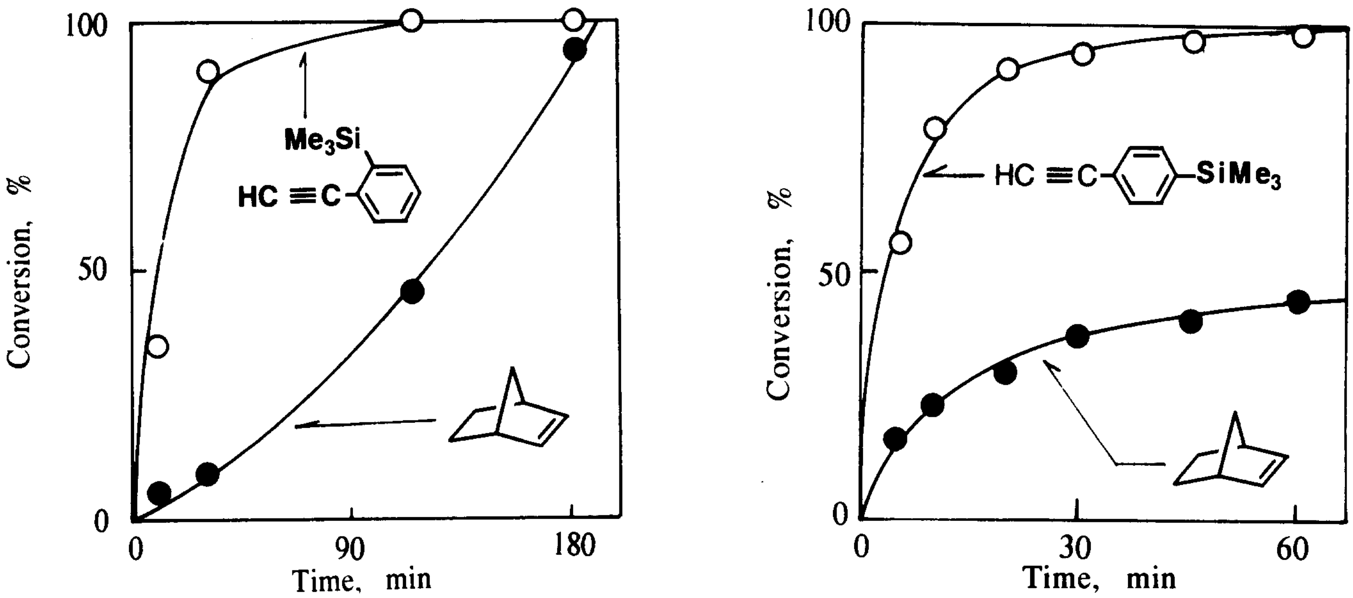


Figure 7 Copolymerization of NBE with *o*- and *p*-Me_3SiPA by WCl_6 (in toluene, 30°C, $[WCl_6] = 10$ mM, $[M_1]_o = [M_2]_o = 0.50$ M)

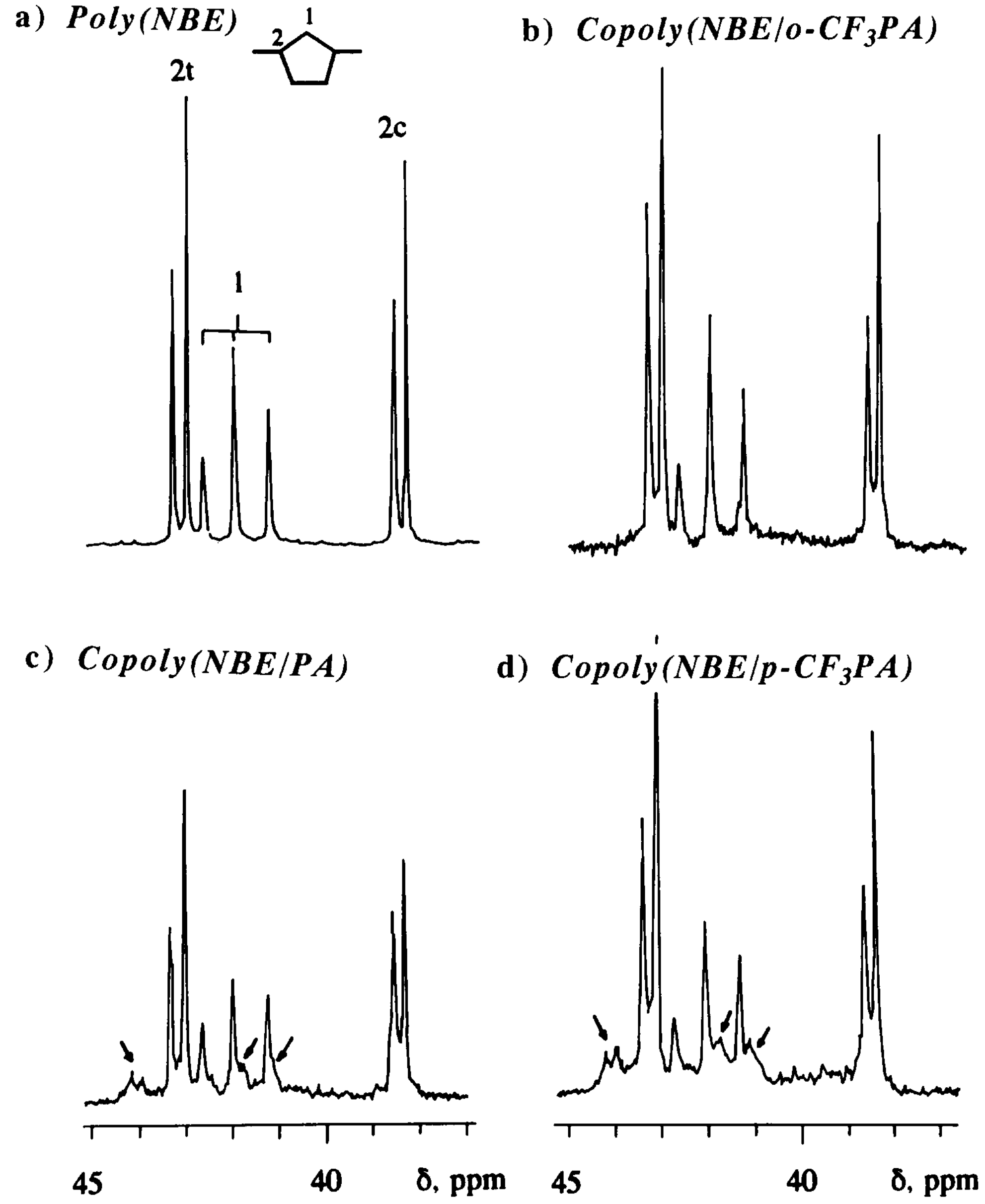


Figure 8 ^{13}C n.m.r. spectra (aliphatic region) of poly(NBE) and copolymers (measured in $CDCl_3$ at 270 MHz)

Confirmation of block character by n.m.r.

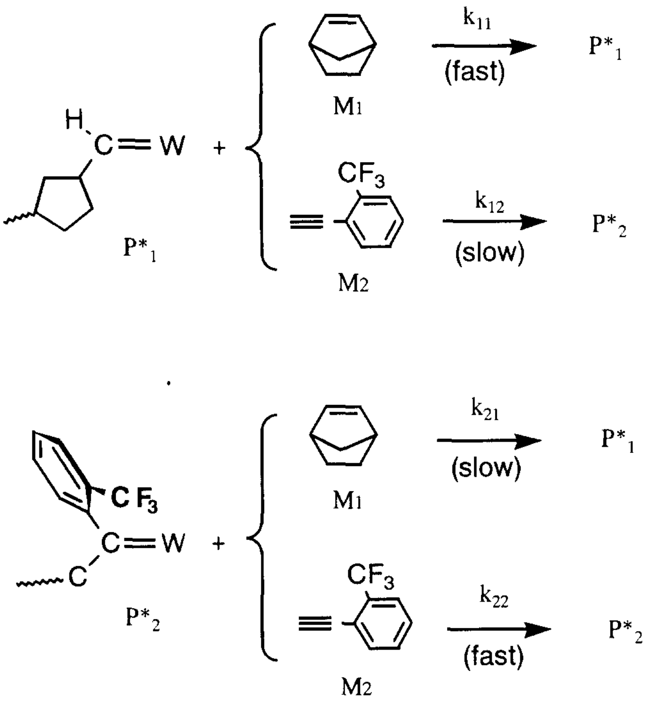
In general, a blocky copolymer should have a smaller amount of cross-propagating dyad than does a random copolymer with the same composition. In the present study, many signals due to a cross-propagating dyad are seen in the aliphatic region of ^{13}C n.m.r. spectra of random copolymers such as copoly(NBE/PA) and copoly(NBE/*p*-CF_3PA) (*Figure 8c* and *d*; shown with arrows). In contrast, copoly(NBE/*o*-CF_3PA) (*Figure 8b*) hardly shows such signals, and its spectrum of the aliphatic region resembles that of the NBE homopolymer (*Figure 8a*). This also demonstrates that copolymers from *ortho*-substituted phenylacetylenes and NBE are more blocky.

On the reason for block character

When the $1/r_{NBE}$ values of the phenylacetylenes with the same substituents (CH_3, Cl, CF_3) at *para*, *meta* and *ortho* positions are compared with one another (see *Table 1*), one will note that the *para*- and *meta*-isomers possess similar values to each other, while the *ortho*-isomers have slightly smaller values. Thus the $1/r_{NBE}$ values tend to decrease consistently as the substituent of PA becomes more electron-withdrawing.

The $r_{PA(X)}$ values of *para*- and *meta*-isomers are close to their $1/r_{NBE}$ values; e.g. $r_{p\text{-}CF_3PA}$ 1.6 *versus* $1/r_{NBE}$ 1.6; $r_{m\text{-}CF_3PA}$ 1.4 *versus* $1/r_{NBE}$ 1.3. In contrast, the $r_{PA(X)}$ value of sterically crowded *ortho*-isomers are much larger than not only their $1/r_{NBE}$ values but also the $r_{PA(X)}$ and $1/r_{NBE}$ values of the corresponding *para*- and *meta*-isomers; e.g. $r_{o\text{-}CF_3PA}$ 5.1 *versus* $1/r_{NBE}$ 0.41. Hence one can conclude that the origin for the formation of blocky copolymers from *ortho*-substituted phenylacetylenes in the unusually large $r_{PA(X)}$ values. Further, the magnitude of $r_{PA(X)}$ value in the copolymerization of *ortho*-isomers with NBE cannot be correlated simply with the electronic factor of *ortho*-substituents, and should be strongly influenced by the steric effect; e.g. r_{PA} 4.8, $r_{o\text{-}ClPA}$ 4.6, $r_{o\text{-}CF_3PA}$ 5.1.

The mechanism of formation of such blocky copolymers is discussed below for the case of NBE(M_1)-*o*-CF_3PA(M_2) copolymerization (*Scheme 2*): The NBE propagating end



Scheme 2

(P_1^*) is a metal carbene whose substituents on the carbon are a hydrogen and a 1,3-cyclopentylene polymer chain. The steric effect of these groups will be small in the propagation reaction. Hence it is attributable to the electron-withdrawing trifluoromethyl group that NBE is more reactive than o-CF_3PA towards the NBE end ($k_{11} > k_{12}$; $r_1 > 1$). On the other hand, the substituents on the carbon of the o-CF_3PA propagating end (P_2^*) are a polymer chain and a phenyl group with a bulky *ortho*-substituent. Further, NBE is an α, β-disubstituted olefin with two *sec*-alkyl groups. Consequently the reaction of the o-CF_3PA end with NBE is sterically rather difficult, which will lead to $k_{22} > k_{21}$, i.e. $r_2 > 1$. This predominance of self-propagation over cross-propagation for both propagating ends should be responsible for the formation of a blocky copolymer.

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