Metathesis copolymerization of norbornene with phenylacetylene and its ring-substituted derivatives catalysed by WCl_6: 1. Product characterization

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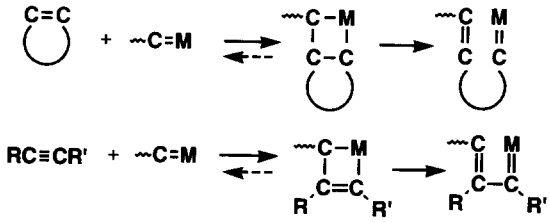
In the copolymerization of phenylacetylene (PA) with norbornene (NBE) catalysed by WCl_6, both monomers reacted simultaneously, the relative reaction rate of PA being several times higher than that of NBE. The product consisted of polymeric (84 wt%, $\overline{M}_n = 41\,000$) and oligomeric (16 wt%, $\overline{M}_n$ = several hundreds) parts. According to g.p.c., u.v. and n.m.r. analyses, the former part was a PA–NBE copolymer, while the latter was a mixture of PA oligomers. The PA–NBE dyads could be directly observed in the 2-D H-H COSY n.m.r. spectrum of the polymeric part. The *p*-CF_3 and *o*-CF_3 derivatives of PA showed reactivities close to that of NBE (relative rates $\sim$1.4:1 and $\sim$1.3:1, respectively). The oligomeric by-products were less in these systems, and the formation of copolymers was similarly confirmed.

(Keywords: metathesis polymerization; copolymerization; phenylacetylene; norbornene; metal carbene; 2-D H-H COSY n.m.r. spectrum)

INTRODUCTION

Group 5 and 6 transition-metal catalysts are effective in the ring-opening metathesis polymerization (ROMP) of cycloolefins, for which a great number of studies have been carried out[1–3]. The active species of this polymerization is metal carbene and the propagation reaction proceeds via metallacyclobutane (*Scheme 1*). In recent studies, well-characterized transition-metal alkylidene complexes have often been used as catalysts[4,5].



Scheme 1

Group 5 and 6 transition-metal catalysts afford high-molecular-weight polymers also from substituted acetylenes[6,7]. Despite a large apparent difference in monomer structure between cycloolefins and substituted acetylenes, this polymerization has also been assumed to proceed with metal carbene as the intermediate, i.e. by the metathesis mechanism (*Scheme 1*)[6–10].

If the metal carbene is a common active species of polymerization for both a cycloolefin and a substituted acetylene, and the monomers as well as their propagating species have similar reactivities, then there is a possibility that random copolymerization occurs between them. If this copolymerization is successful, it will support the metal carbene mechanism for the polymerization of substituted acetylenes, and will provide a novel type of copolymer.

In the present study, we investigated the copolymerization of a cycloolefin with substituted acetylenes[11]. Bicyclo-[2.2.1]hept-2-ene (norbornene; NBE), which is very reactive in ROMP, was used as the cycloolefin. Phenylacetylene (PA), *p*-(trifluoromethyl)phenylacetylene (*p*-CF_3PA), *o*-(trifluoromethyl)phenylacetylene (*o*-CF_3PA) and some other PAs were used as the substituted acetylenes. *p*-CF_3PA is expected to be less reactive than PA because of the presence of an electron-withdrawing substituent[12], and *o*-CF_3PA should show not only electronic but also steric effects due to the CF_3 group[13]. WCl_6 was employed as the catalyst because it exhibited a moderate activity.

EXPERIMENTAL

Materials

PA was commercially obtained. Ring-substituted PAs (*p*-CF_3PA, *o*-CF_3PA, etc.) were prepared with reference to literature methods[14] through Pd-catalysed coupling of the corresponding iodobenzenes with 2-methyl-3-butyn-2-ol followed by base-catalysed acetone elimination. Phenyl-d_5-acetylene (PA-d_5) was prepared in the same way from iodobenzene-d_5 which was synthesized[15] by direct iodination of benzene-d_6. The monomers prepared were identified by i.r. and n.m.r.

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spectroscopies. These acetylenes were all distilled twice from calcium hydride at reduced pressure before use; purities were >99% according to g.c. Commercial NBE was distilled twice from calcium hydride under dry nitrogen (purity >99% by g.c.), and stored as a toluene solution (5.0 M). Toluene as polymerization solvent was purified by a standard method. WCl_6 (Furuuchi Chemicals, Japan; purity >99.9%) was commercially obtained and used without further purification.

Procedures

Copolymerization was carried out under dry nitrogen in a prebaked flask equipped with a three-way stopcock. The polymerization conditions were: in toluene, at 30°C, $[M]_{0,total} = 1.0$ M, $[WCl_6] = 10$ mM. The catalyst solution was aged at 30°C for 15 min before use. The polymerization reaction was initiated by adding a monomer solution to this catalyst solution, and quenched after a given time by adding a mixture of isobutyl alcohol and toluene (1:4 volume ratio). The conversion of both monomers was determined by measuring the initial and final monomer concentrations by g.c. The copolymerization products for characterization were prepared by keeping the conversion of a more reactive comonomer to 80–90% since the exclusive formation of a random copolymer is rather difficult after such a point. The copolymerization products were isolated by precipitation of reaction mixtures into a large amount of methanol, filtered off and dried to constant weights under vacuum at room temperature, and employed for various analyses. For g.p.c., however, the whole reaction products were used, which were isolated by evaporation of the solvent and residual monomer, dissolution in toluene, washing with water and evaporation of toluene.

Product characterization

The g.p.c. analyses were performed with a Jasco Trirotar liquid chromatograph. Usually a series of Shodex A803, A804 and A805 polystyrene gel columns were used, but a series of A805, A806 and A807 columns were used for high-molecular-weight polymers (Showa Denko Co., Japan). The eluent was $CHCl_3$, and refractive index/u.v. (r.i./u.v.) dual detectors were used with polystyrene calibration. I.r. spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. U.v.-visible spectra were measured with a Shimadzu UV2200 spectrophotometer at room temperature usually in CCl_4. The spectra of poly(*p*-CF_3PA) and poly(NBE), however, were measured in tetrahydrofuran because they did not dissolve in CCl_4. 1-D ^1H and 2-D H-H COSY n.m.r. spectra were observed on a JEOL GSX270 spectrometer in $CDCl_3$ solution at room temperature.

RESULTS AND DISCUSSION

Copolymerization of PA with NBE

Figure 1 shows time–conversion curves for the copolymerization of PA with NBE at a 1:1 feed ratio. Both monomers were consumed smoothly without any induction period. The reactivity of PA was several times higher than that of NBE. The product of copolymerization for 45 min was used as the sample for the analyses stated below. At this point, the conversions of PA and NBE were 92 and 42%, respectively. The whole product was used for g.p.c. analysis, while the methanol-insoluble part (84 wt%) was used for the other analyses.

Figure 2 shows the g.p.c. curves of the product. It is clear from this figure that the product consists of high- and low-molecular-weight parts. The former occupied 82% of the whole area according to the r.i. detector, which corresponded well to the methanol-insoluble fraction of the product. The number-average molecular weight ($\overline{M}_n$) and polydispersity ratio ($\overline{M}_w/\overline{M}_n$) of the high-molecular-weight part were 41 000 and 2.15, respectively. The low-molecular-weight part mainly consisted of the cyclotrimers and by-products (not identified) from PA. The high-molecular-weight part (main product) showed an identical molecular weight distribution irrespective of the r.i. and u.v. (350 nm) detectors. This indicates uniform distribution of the two monomer units, since both poly(PA) and poly(NBE) sequences are observed by the r.i. detector, while only the poly(PA) sequence is observed by the u.v. detector.

The i.r. spectrum of the copolymerization product exhibited key absorptions due to both PA and NBE units; e.g. C-H out-of-plane deformations at 755 and 693 cm^{-1}, and their overtones in the range 2000–1660 cm^{-1} for the former unit, and C-H stretchings of saturated CH, CH_2 at 2950–2800 cm^{-1} for the latter. ^1H and ^{13}C n.m.r. spectra also showed the presence of both PA and NBE units.

Figure 3 illustrates the u.v.-visible spectrum of the copolymerization product. For the sake of comparison, a curve is shown which was obtained by multiplying the spectrum of poly(PA) by the mole fraction of PA (0.67)

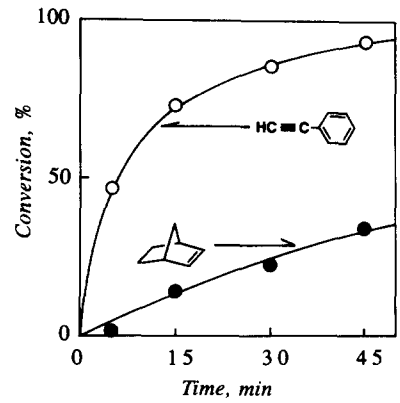


Figure 1 Copolymerization of PA with NBE by WCl_6 (in toluene, 30°C, $[WCl_6] = 10$ mM, $[PA]_0 = [NBE]_0 = 0.50$ M)

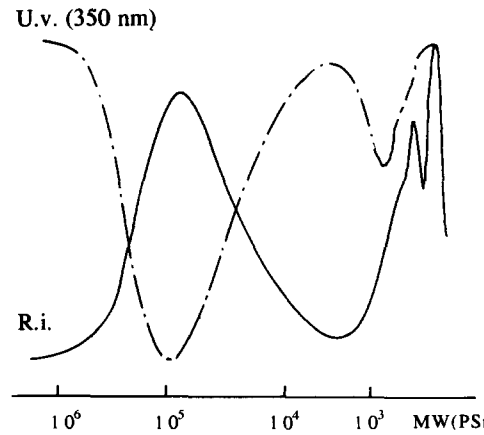
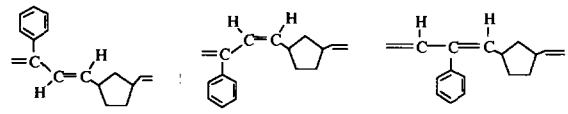


Figure 2 Molecular weight distribution curves of the product in PA–NBE copolymerization (sample: the product at 45 min in *Figure 1*)

in the copolymerization product. Since poly(NBE) possesses no absorption above 300 nm, this curve can be regarded as the spectrum of a homopolymer mixture which has the same composition as the copolymerization product. Obviously, the absorption of the copolymerization product is stronger below 390 nm but weaker above 390 nm than that of the reference curve. This indicates the presence of less conjugated poly(PA) sequences in the copolymerization product due to the intervention of NBE units. Corresponding to the u.v.-visible spectra, the copolymerization product was an orange-coloured solid, whereas poly(PA) and poly(NBE) are dark red and white, respectively.

The 2-D H-H COSY n.m.r. spectrum of the product exhibited four kinds of correlation peaks (*Figure 4*). Among them, peak *p* (intersection of δ 6.5 and 5.5) and peak *q* (intersection of δ 6.1 and 5.1) are attributable to the cross-propagating structure I (*trans*) and II (*cis*), respectively. These assignments are reasonable because the *trans* and *cis* olefinic protons of poly(PA-d_5) prepared by WCl_6 appeared broadly at δ 6.3 and 5.8, respectively, in the present study, while the *trans* and *cis* structures of poly(NBE) should correspond to the peaks at δ 5.3 and 5.2, respectively. Here the peak assignments for homopolymers are supported by the data of Furlani *et al.*[16] for poly(PA-d_5) and by the data of Ivin *et al.* for ^{13}C signals[17] in conjunction with the C-H COSY n.m.r. spectrum measured by us for poly(NBE). Naturally, each homopolymer does not show the correlation peaks. Thus the 2-D n.m.r. spectrum enables us to directly observe the double bonds between PA and NBE units.

In order to confirm the assignment of correlation peaks, we examined the H-H COSY n.m.r. spectrum of a copoly(PA-d_5–NBE) whose PA-d_5 content was <5 mol% (*Figure 5*). The spectrum obtained is highly resolved, in which correlation peaks *p* and *q* are split into a triplet or quartet for the NBE proton and into a doublet for the PA-d_5 proton. This agrees with structures I and II. Peak *q* consists of two groups of peaks, suggesting that the two kinds of *cis* structures exist. Several peaks in 1-D ^1H n.m.r. between δ 5.9 and 5.5 may be attributable to another dyad structure (structure III). The two weaker correlation peaks at the intersection of δ 6.9 and 6.1 and at the intersection of δ 7.0 and 5.3 are not identifiable at present.



I (peak *p*) II (peak *q*) III

All these observations in g.p.c., u.v.-visible, i.r. and 2-D n.m.r. spectroscopies manifest that the product of this copolymerization is a copolymer and not a mixture of homopolymers.

Copolymerization of p-CF_3*PA with NBE*

It is known that *p*-chlorophenylacetylene, which has an electron-withdrawing substituent, is less reactive than PA in copolymerization[12]. Thus, copolymerization of *p*-CF_3PA with NBE was examined in order to find a PA derivative whose reactivity is closer to NBE. In the copolymerization of these monomers at a 1:1 feed ratio, both monomers were consumed simultaneously (*Figure 6a*). As expected, *p*-CF_3PA was less reactive than PA,

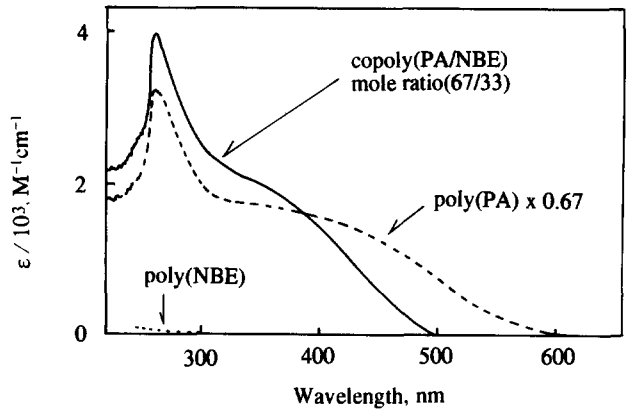


Figure 3 U.v.-visible spectra of the products in PA–NBE co- and homopolymerizations (sample of copolymerization: the product at 45 min in *Figure 1*)

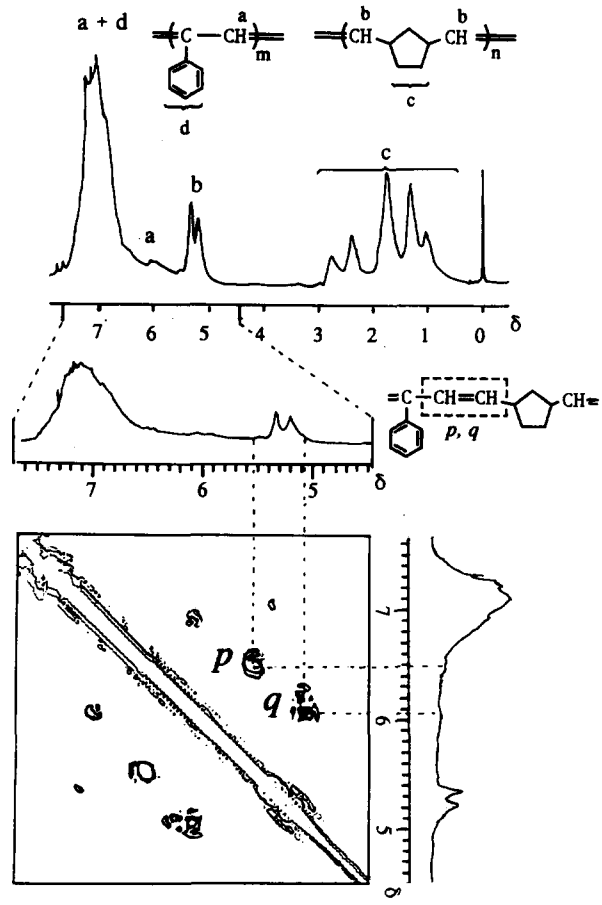


Figure 4 1-D ^1H and 2-D H-H COSY n.m.r. spectra of the product in PA–NBE copolymerization (sample: the product at 45 min in *Figure 1*; 270 MHz, in $CDCl_3$)

and close to NBE in reactivity (relative reaction rate of *p*-CF_3PA to NBE was ~1.4:1 on average). The product in this copolymerization at 10 min was used in the following analyses.

As seen in *Figure 7a*, the g.p.c. curve based on an r.i. detector of the whole copolymerization product consisted of high-molecular-weight (~95%) and low-molecular-weight (~5%) parts. The $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of the high-molecular-weight, methanol-insoluble part were 82000 and 2.40, respectively. The low-molecular-weight,

methanol-soluble part consisted of the cyclotrimers and unidentifiable by-products from p-CF_3PA. The high-molecular-weight product displayed an identical elution curve with both r.i. and u.v. (350 nm) detectors, and showed absorptions assignable to both monomer units in the i.r. spectrum.

The u.v.-visible spectrum of the methanol-insoluble product exhibited a blue shift which is clearer than that in the PA–NBE copolymer (*Figure 8a*). This again demonstrates the interruption of main-chain conjugation by NBE units. Accordingly, the product was yellow in contrast to the reddish-purple colour of poly(p-CF_3PA).

The H-H COSY n.m.r. spectrum showed four kinds of correlation peaks whose positions were similar to those of the PA–NBE copolymer (*Figure 9a*). Peaks *p* and *q* can be assigned to *trans* and *cis* cross-propagating structures, respectively. These peaks strongly support the existence of p-CF_3PA–NBE dyad.

The above data indicate that p-CF_3PA and NBE also copolymerize in the presence of WCl_6 through the metathesis mechanism.

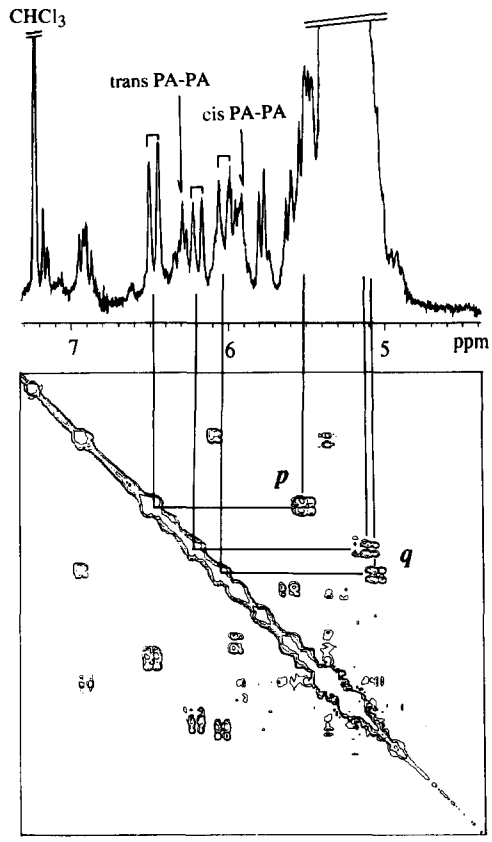


Figure 5 H-H COSY n.m.r. spectrum of the product in PA-d_5-NBE copolymerization (sample: obtained in toluene, 30°C, 10 min, $[WCl_6]=10$ mM, $[PA\text{-}d_5]_0=0.10$ M, $[NBE]_0=0.90$ M; 270 MHz, in $CDCl_3$)

Copolymerization of o-CF_3PA with NBE

Ortho-substituted PAs are characterized by the formation of high-molecular-weight polymers ($\overline{M}_w=\sim 1\times 10^6$) as well as interesting polymer properties[18–20]. Thus it is interesting to study copolymerization of NBE with an *ortho*-substituted PA. o-CF_3PA, which has an electron-withdrawing group, was used as the *ortho*-substituted PA for the same reason as p-CF_3PA.

Figure 6b shows time–conversion curves for the copolymerization of o-CF_3PA with NBE at a 1:1 feed ratio. Both monomers were consumed at similar rates, which resembles the combination of p-CF_3PA and NBE (relative reaction rate of o-CF_3PA to NBE was ~1.3:1 on average). The consumption rates of these monomers were much smaller than those of p-CF_3PA and NBE perhaps because of the steric hindrance of the *ortho* substituent. The product after polymerization for 180 min (monomer conversion: o-CF_3PA 76%, NBE 65%) was employed for the following examinations.

Interestingly, the product of this copolymerization consisted of the polymeric part only, and no oligomeric part was found in the g.p.c. curve. It is noted that the amounts of the methanol-soluble, oligomeric by-products (18% for PA–NBE, 5% for p-CF_3PA–NBE, 0% for o-CF_3PA–NBE) are virtually the same, respectively, as those in the homopolymerization of these PA derivatives[18–20]. The g.p.c. curve was unimodal irrespective of r.i. and u.v. (350 nm) detectors (*Figure 7b*). The $\overline{M}_n$ of the polymeric, methanol-insoluble product was 159 000, and its $\overline{M}_w/\overline{M}_n=3.14$.

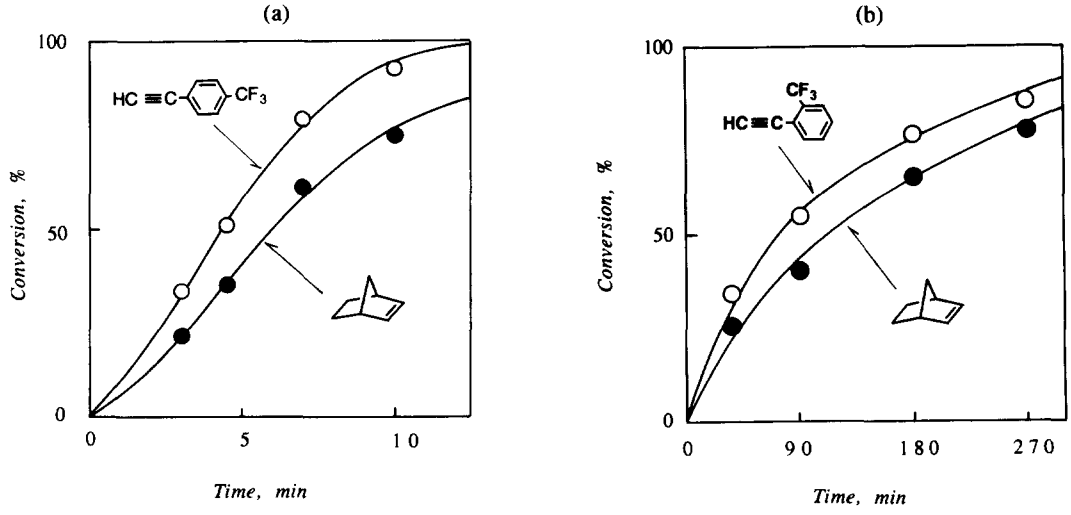


Figure 6 Copolymerizations of trifluoromethyl derivatives of PA [(a) p-CF_3PA and (b) o-CF_3PA] with NBE by WCl_6 (in toluene, 30°C, $[WCl_6]=10$ mM, $[p$- or o-$CF_3PA]_0=[NBE]_0=0.50$ M)

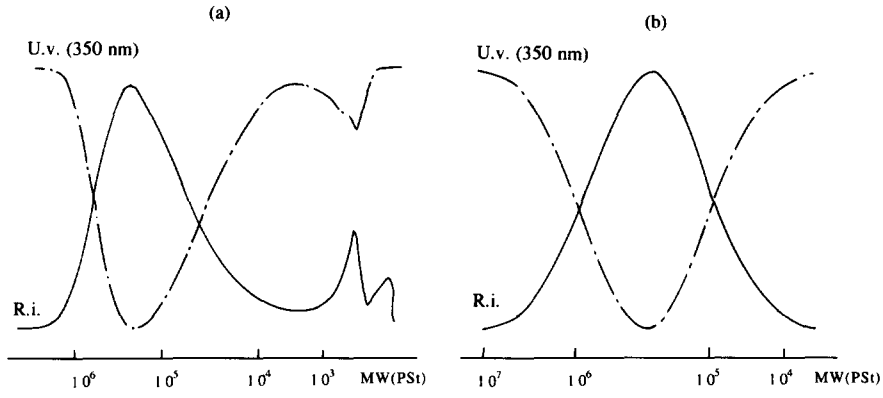


Figure 7 Molecular weight distribution curves of the products in copolymerizations of trifluoromethyl derivatives of PA [(a) *p*-CF_3PA and (b) *o*-CF_3PA] with NBE (samples: the product at 10 min in *Figure 6a* and that at 180 min in *Figure 6b*, respectively)

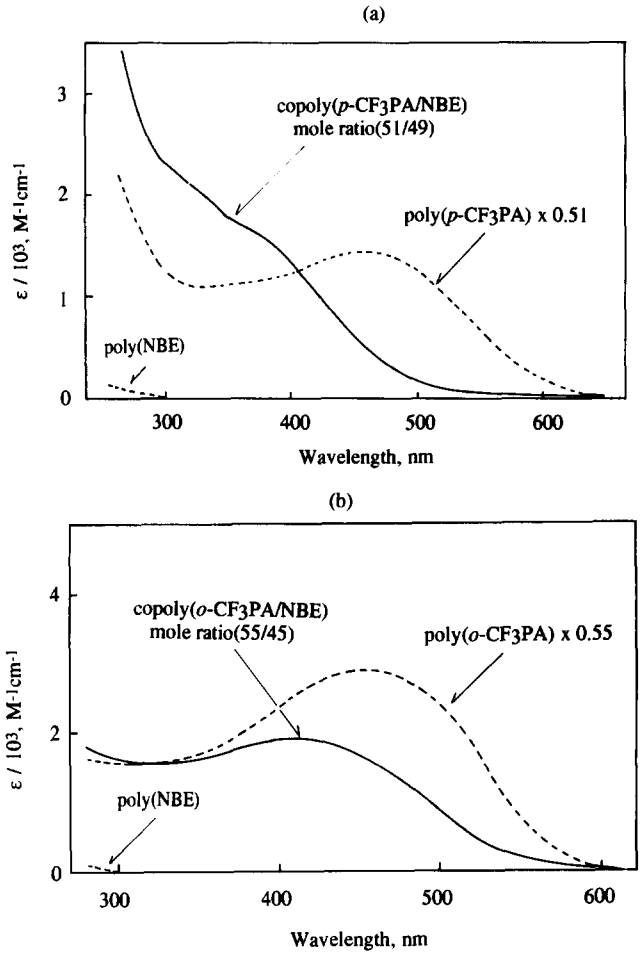


Figure 8 U.v.-visible spectra of the products in co- and homopolymerizations of trifluoromethyl derivatives of PA [(a) *p*-CF_3PA and (b) *o*-CF_3PA] with NBE (samples of copolymerization: the product at 10 min in *Figure 6a* and that at 180 min in *Figure 6b*, respectively)

In general, *ortho*-substituted poly(PA)s show fairly large absorption maxima in the visible region[18–20] and not in the u.v. region. The polymeric product of *o*-CF_3PA–NBE copolymerization also showed an absorption maximum in the visible region. Its absorption, however, shifted towards short wavelengths as compared with that of homopoly(*o*-CF_3PA) (*Figure 8b*). This is also attributable to a shorter conjugation length of the main chain in the copolymerization product. The product was

Table 1 Chemical shifts (δ) of correlation peaks in the 2-D H-H COSY n.m.r. spectra of copoly(PA(X)–NBE)[a]

Substituents X	*trans* (peak *p*)		*cis* (peak *q*)	
	$H_{PA(X)}$	H_{NBE}	$H_{PA(X)}$	H_{NBE}
None	6.50	5.50	6.03 6.19	5.05 5.10
p-CF_3	6.50	5.49	5.95 6.22	5.07 5.07
p-Cl	6.46	5.45	5.95 6.16	5.07 5.07
p-CH_3	6.42	5.48	6.05 6.16	5.04 5.10
o-CF_3	6.55	4.97	6.22	4.74
o-Cl	6.48	5.09	6.15	4.86
o-CH_3	6.48	5.07	6.17	4.87

[a] Recorded at 270 MHz in $CDCl_3$ with internal Me_4Si as reference

an orange-coloured solid (cf. poly(*o*-CF_3PA), a dark red solid).

The H-H COSY n.m.r. spectrum of the polymeric product exhibited two correlation peaks based on cross-propagation dyads (*Figure 9b*). Consequently one can conclude that the copolymerization of *o*-CF_3PA with NBE also forms a copolymer.

The H-H COSY n.m.r. spectrum of copoly(*o*-CF_3PA–NBE) (*Figure 9b*) possesses the following features as compared with those of copoly(PA–NBE) and copoly(*p*-CF_3PA–NBE) (*Figures 4*, *5* and *9a*): the olefinic protons, especially the one in the *trans* form, of the NBE unit adjacent to the *o*-CF_3PA unit, appear appreciably upfield; and peak *q* is composed of a single peak. In order to examine the generality of these observations, the chemical shifts of correlation peaks of the copolymers from various ring-substituted PAs with NBE were studied (*Table 1*). *Table 1* shows that these observations are common in the copolymers of *ortho*-substituted PAs with NBE and that the upfield shifts of H_{NBE} are caused by the steric factor (whether *ortho* substituents or not) rather than the electronic factor.

A particular conformation due to the presence of bulky *ortho* substituents seems responsible for the above observations. It is likely that poly(PA)s with *ortho*

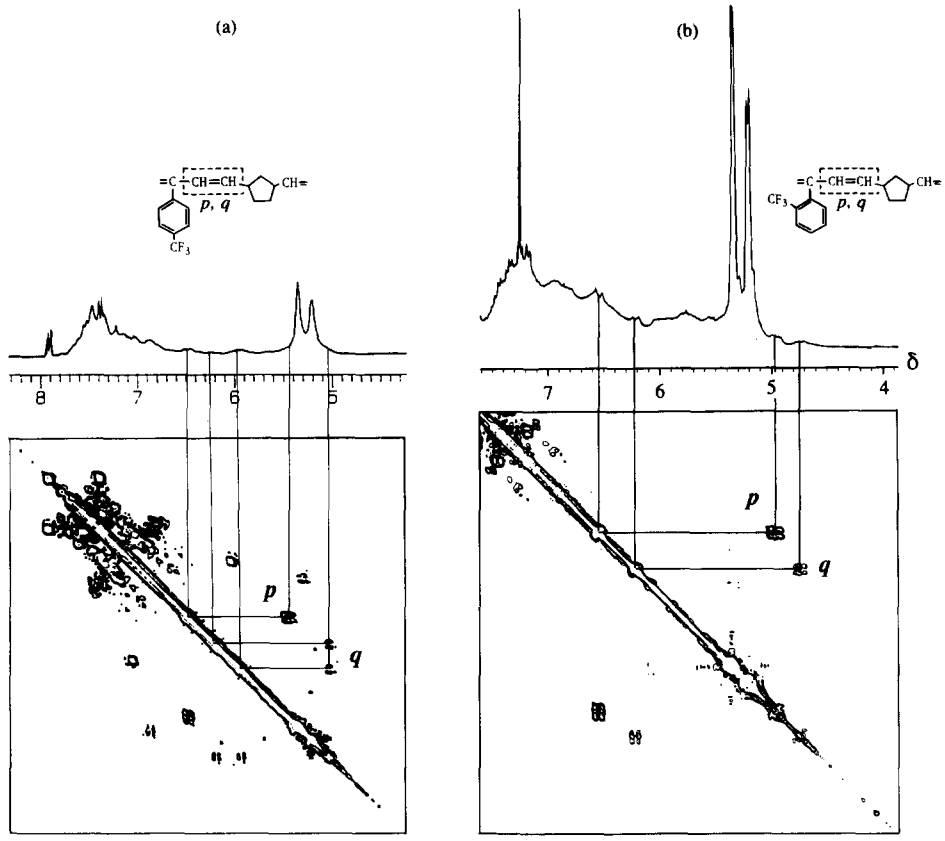


Figure 9 H-H COSY n.m.r. spectra of the products in copolymerizations of trifluoromethyl derivatives of PA [(a) *p*-CF_3PA and (b) *o*-CF_3PA] with NBE (samples: the product at 10 min in *Figure 6a* and that at 180 min in *Figure 6b*, respectively; 270 MHz, in $CDCl_3$)

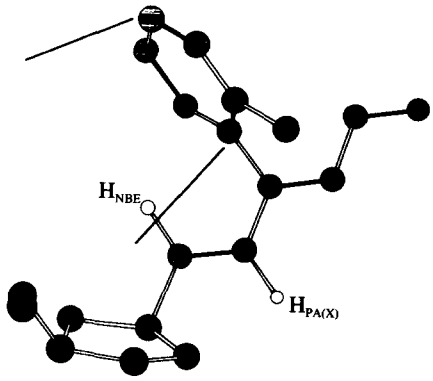


Figure 10 Probable PA–NBE dyad conformation of copoly(*ortho*-substituted PA–NBE)

substituents assume a conformation in which the phenyl group is almost perpendicular to the main chain and in which the main chain is fairly planar. On the basis of these considerations, one can depict a polymer conformation as shown in *Figure 10*, which rationalizes the upfield shift of H_{NBE} due to the shielding effect of the phenyl group.

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REFERENCES

1 Ivin, K. J. 'Olefin Metathesis', Academic Press, London, 1983
2 Dragutan, V., Balaban, A. T. and Dimonie, M. 'Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins', Wiley, Chichester, 1985
3 Amass, A. J. and Feast, W. J. in 'Comprehensive Polymer Science', Vol. 4, Pergamon Press, Oxford, 1989, Chs 6 and 7
4 Schrock, R. R. *Acc. Chem. Res.* 1990, **23**, 158
5 Grubbs, R. H. *Science* 1989, **243**, 1907
6 Costa, G. in 'Comprehensive Polymer Science', Vol. 4, Pergamon Press, Oxford, 1989, Ch. 9
7 Masuda, T. and Higashimura, T. *Adv. Polym. Sci.* 1986, **81**, 121
8 Katz, T. J. and Lee, S. J. *J. Am. Chem. Soc.* 1980, **102**, 422
9 Katz, T. J., Lee, S. J., Nair, M. and Savage, E. B. *J. Am. Chem. Soc.* 1980, **102**, 7942
10 Han, C.-C. and Katz, T. J. *Organometallics* 1985, **4**, 2186
11 Masuda, T., Yoshida, T., Makio, H., Rahman, M. Z. A. and Higashimura, T. *J. Chem. Soc., Chem. Commun.* 1991, 503
12 Hasegawa, K., Masuda, T. and Higashimura, T. *Macromolecules* 1975, **8**, 255
13 Masuda, T., Yoshizawa, T. and Higashimura, T. *Polymer* 1984, **25**, 503
14 Carpita, A., Lessi, A. and Rossi, R. *Synthesis* 1984, 571
15 Suzuki, H., Nakamura, K. and Goto, R. *Bull. Chem. Soc. Jpn* 1966, **39**, 128
16 Furlani, A., Napoletano, C., Russo, M. V. and Feast, W. J. *Polym. Bull.* 1986, **16**, 311
17 Ivin, K. J., O'Donnell, J. H., Rooney, J. J. and Stewart, C. D. *Makromol. Chem.* 1979, **180**, 1975
18 Masuda, T., Hamano, T., Higashimura, T., Ueda, T. and Muramatsu, H. *Macromolecules* 1988, **21**, 281
19 Abe, Y., Masuda, T. and Higashimura, T. *J. Polym. Sci., Polym. Chem. Edn* 1989, **27**, 4267
20 Masuda, T., Hamano, T. and Higashimura, T. *Macromolecules* 1990, **23**, 1374