polymer report

Polymerization and polymer properties of diarylacetylenes

Hiroaki Kouzai, Toshio Masuda* and Toshinobu Higashimura
Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan
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The polymerization of three diarylacetylenes, namely 1-(*p*-benzylphenyl)-2-phenylacetylene (*p*-BzDPA), 1-(*p*-phenylphenyl)-2-phenylacetylene and 1-(β-naphthyl)-2-phenylacetylene, was examined. These monomers polymerized in good yields with $TaCl_5$–cocatalyst systems. Poly(*p*-BzDPA) was soluble in various organic solvents and had high molecular weights of 6×10^5–9×10^5 according to gel permeation chromatography. In contrast, the other two polymers were insoluble in all solvents. All these polymers had fairly good thermal stability in air (their onset temperatures of weight loss in air were 330–450°C). The oxygen permeability coefficient of poly(*p*-BzDPA) at 25°C was 18 barrers, which was close to that of natural rubber (23 barrers).

(Keywords: poly(diarylacetylene); metathesis polymerization; tantalum catalyst)

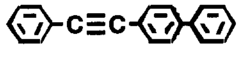
INTRODUCTION

Among the various substituted acetylenes, diphenylacetylene (DPA) polymerizes in good yields with $TaCl_5$–cocatalyst systems, and the polymer obtained has high thermal stability (the onset temperature of weight loss in air, T_0, is $\sim 500°C$)[1]. However, it has the drawback that it does not dissolve in any solvent.

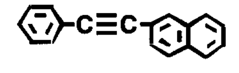
In a previous paper[2], we reported the synthesis of new polymers from 1-(*p*-t-butylphenyl)-2-phenylacetylene (*p*-t-BuDPA) and 1-(*p*-n-butylphenyl)-2-phenylacetylene (*p*-n-BuDPA). These polymers were soluble in various organic solvents, and their weight-average molecular weights ($\bar{M}_w$) measured by gel permeation chromatography (g.p.c.) exceeded 1×10^6. They also had fairly good thermal stability ($T_0 = 320$–$380°C$).

It is anticipated that DPAs having mostly or exclusively aromatic groups show different properties, especially higher thermal stability, as compared with the alkyl-containing counterparts. Thus the polymerization and polymer properties of 1-(*p*-benzylphenyl)-2-phenylacetylene (*p*-BzDPA), 1-(*p*-phenylphenyl)-2-phenylacetylene (*p*-PhDPA) and 1-(β-naphthyl)-2-phenylacetylene (β-NPA) were investigated in the present study. The results are discussed in comparison with those of DPAs having an aliphatic[2] or a silyl[3] group as *para*-substituent.

***p*-BzDPA**



***p*-PhDPA**



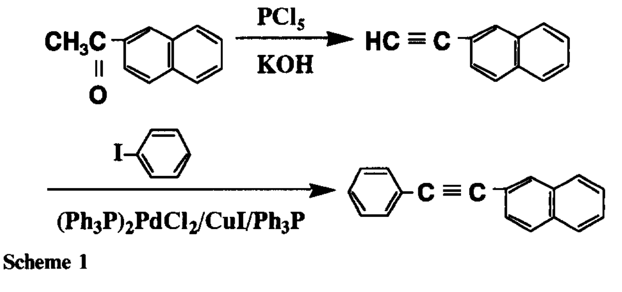
β-NPA

EXPERIMENTAL

Materials

p-BzDPA and *p*-PhDPA (new compounds) were prepared by the methods described in a previous paper[2]; i.e. *p*-BzDPA was synthesized by the Sandmeyer reaction of 4-aminodiphenylmethane followed by Pd-catalysed coupling with phenylacetylene[4,5]. The crude product was purified by recrystallization from a methanol–water (5:1) mixture. *p*-BzDPA: m.p. 90–91°C, yield 47%, purity >99.9% (by gas chromatography). I.r. (KBr) 3027(m), 2200(m, $\nu_{C\equiv C}$), 1509(m), 1451(m), 1105(m), 1071(m), 793(m), 758(s), 737(m), 723(m) and 693(s) cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ 7.6–7.1 (aromatic) and 3.9 (s, 2, $-CH_2-$) ppm. ^{13}C n.m.r. ($CDCl_3$) δ 141.4, 140.4, 131.6, 131.5, 128.9, 128.8, 128.4, 128.2, 128.0, 126.1, 123.3, 120.9, 89.3, 89.0 and 41.7 ppm. *p*-PhDPA was prepared in a similar way from 4-iodobiphenyl, which was synthesized through iodination of biphenyl[6], and recrystallized from a methanol–water (5:1) mixture. *p*-PhDPA: m.p. 145–146°C, yield 45%, purity >99.9% (g.c.). I.r. (KBr) 3034(m), 2208(m, $\nu_{C\equiv C}$), 1539(m), 1491(s), 1441(m), 1404(m), 1167(m), 1071(m), 1007(m), 912(m), 839(s), 754(s) and 718(s) cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ 7.7–7.1 (aromatic) ppm. ^{13}C n.m.r. ($CDCl_3$) δ 140.9, 140.4, 131.9, 131.6, 128.8, 128.3, 128.2, 127.5, 126.9, 123.4, 122.3, 90.1 and 89.4 ppm.

β-NPA (a new compound) was prepared according to *Scheme 1* and purified by recrystallization in the same



Scheme 1

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* To whom correspondence should be addressed

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Table 1 Polymerization of *p*-BzDPA by various catalysts[a]

Catalyst	Polymer[b]			
	Yield (%)	$10^3\ \bar{M}_w$ g.p.c.	$10^3\ \bar{M}_w$ l.s.	$10^3\ \bar{M}_n$ g.p.c.
$TaCl_5$	0	–	–	–
$TaCl_5$–n-Bu_4Sn	74	870	430	350
$TaCl_5$–Et_3SiH	68	950	600	430
$TaCl_5$–9BBN[c]	66	620	330	250
$TaCl_5$–Ph_4Sn	5	320	–	160
$NbCl_5$–n-Bu_4Sn	0	–	–	–
WCl_6–n-Bu_4Sn	0	–	–	–
$MoCl_5$–n-Bu_4Sn	0	–	–	–

[a] Polymerized in toluene at 80°C for 6 h; $[M]_0 = 0.20$ M, [Cat] = 20 mM, [Cocat] = 40 mM; the monomer conversions were all 100%

[b] Methanol-insoluble product

[c] 9BBN: 9-borabicyclo[3.3.1]nonane

way[5,7]. β-NPA: m.p. 110–112°C, yield 52%, purity >99.9% (g.c.). I.r. (KBr) 3017(m), 2213(m, $\nu_{C\equiv C}$), 1599(m), 1441(m), 1269(m), 1071(m), 951(m), 914(m), 905(m), 866(s), 823(s), 756(s) and 745(s) cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ 8.1–7.1 (aromatic) ppm. ^{13}C n.m.r. ($CDCl_3$) δ 133.1, 132.8, 131.6, 131.4, 128.4, 128.3, 128.2, 127.9, 127.7, 126.6, 126.5, 123.4, 120.7, 89.9 and 89.8 ppm.

Transition-metal chlorides and organometallic cocatalyts were obtained from commercial sources and used without further purification. Polymerization solvents were purified by the standard methods[8].

Procedures

Polymerizations were carried out as described previously[2]. Monomer conversions were determined by gas chromatography. Molecular weights of polymers were determined by g.p.c. (eluent, $CHCl_3$, polystyrene calibration) and by laser light scattering (in toluene, $\lambda = 633$ nm; angles = 30–70°; four-concentration measurements; $c = 1.9 \times 10^{-5}$–7.7×10^{-5} g ml^{-1}). The refractive index increment (d*n*/d*c*) of poly(*p*-BzDPA) was 0.1942 ml g^{-1}.

Measurements of i.r., n.m.r. and u.v.–visible spectra, thermogravimetric analysis (t.g.a.) and gas permeabilities were carried out in the same manner as described elsewhere[1]. Poly(*p*-BzDPA): calculated for $(C_{21}H_{16})_n$: C, 94.0; H, 6.0; found: C, 93.3; H, 5.8. I.r. (KBr) 2919(m), 1943(m), 1732(m), 1601(s), 1509(m), 1493(m), 1453(m), 1408(s), 1289(m), 1183(m), 1109(s) and 1075(s) cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ 7.8–5.8 (aromatic) and 4.0 (s, 2, CH_2) ppm. ^{13}C n.m.r. ($CDCl_3$) δ 148–122 (aromatic) and 29.7 ppm.

RESULTS AND DISCUSSION

Polymerization of p-*BzDPA*

The polymerization of *p*-BzDPA was examined by using various catalysts (*Table 1*). Mixtures of $TaCl_5$ with organometallic cocatalysts carrying aliphatic groups (e.g. n-Bu_4Sn, Et_3SiH and 9BBN) at a 1:2 ratio are known to serve as effective catalysts in the polymerization of DPA[1]. When these mixtures were used, the monomer polymerized quantitatively, and polymers were obtained in over 60% yields. This result is similar to those for *p*-t-BuDPA and *p*-n-BuDPA[2].

The formed polymers dissolved completely in various organic solvents owing to the presence of the *p*-benzyl group. The absolute $\bar{M}_w$ values, determined by light scattering (l.s.), were about 3×10^5–6×10^5. In contrast, the relative $\bar{M}_w$ values determined by g.p.c. *versus* polystyrene standards reached about 6×10^5–9×10^5, being 1.5–2 times the values by l.s. A similar relationship was observed with other substituted poly(DPA)s[2]. This tendency is explained by the fact that the present polymer is more rigid than polystyrene, and assumes a more expanded conformation in solution.

Ph_4Sn was not as effective as the above-mentioned cocatalysts for other DPAs. According to g.p.c. the main products were linear oligomers, which are presumed to form by a different mechanism from that for polymerization. Steric and mechanistic reasons for Ph_4Sn being ineffective are conceivable but not conclusive. Neither $NbCl_5$-, WCl_6- nor $MoCl_5$-based catalysts produced any methanol-insoluble polymer; this appears to be a general tendency for various DPAs[2,3].

Under the conditions shown in *Figure 1*, the *p*-BzDPA monomer reacted quantitatively within 6 h; then the yield of the methanol-insoluble polymer was about 70% and $\bar{M}_w = 8 \times 10^5$. The polymer molecular weight did not decrease even though the polymerization system was left over 24 h, indicating that polymer degradation did not occur. The molecular weight of the polymer hardly depended on monomer conversion.

To clarify the influence of the *p*-benzyl group on the monomer reactivity, copolymerization of *p*-BzDPA with DPA was carried out with $TaCl_5$–n-Bu_4Sn catalyst in toluene (*Figure 2*). *p*-BzDPA was consumed faster than DPA. This seems to be due to the electron-donating nature of the *p*-benzyl group.

Polymerization of p-*PhDPA and β-NPA*

Polymerizations of *p*-PhDPA and β-NPA were examined (*Tables 2* and *3*). When $TaCl_5$–cocatalyst systems (cocatalysts: n-Bu_4Sn, Et_3SiH and 9BBN) were used, *p*-PhDPA gave rise to methanol-insoluble polymers in good yields, while β-NPA gave such polymers in moderate yields. Both of these polymers were,

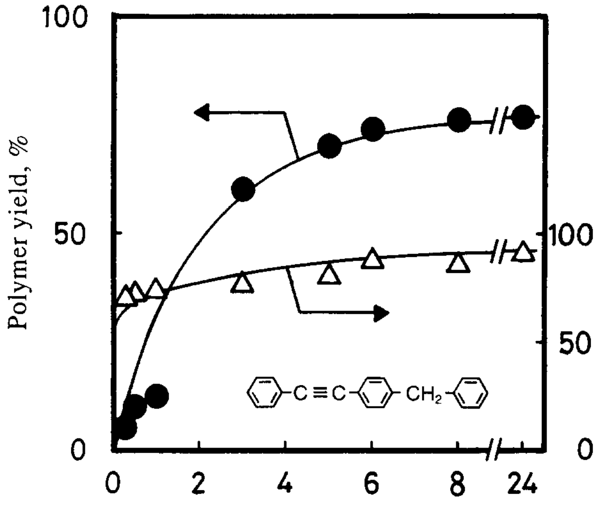

Figure 1 Time profile of the polymerization of *p*-BzDPA by $TaCl_5$–n-Bu_4Sn (in toluene, 80°C, $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, [n-Bu_4Sn] = 40 mM; $\bar{M}_w$ by g.p.c.)

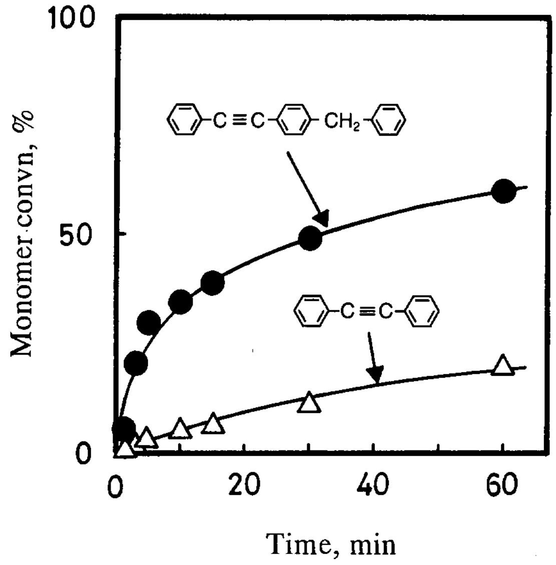

Figure 2 Copolymerization of *p*-BzDPA with DPA by $TaCl_5$–n-Bu_4Sn (in toluene, 80°C, $[M_1]_0=[M_2]_0=0.10$ M, $[TaCl_5]=20$ mM, [n-Bu_4Sn] = 40 mM)

Table 2 Polymerization of *p*-PhDPA by various catalysts[a]

Catalyst	Monomer conversion (%)	Polymer yield[b] (%)
$TaCl_5$	100	0
$TaCl_5$–n-Bu_4Sn	100	82
$TaCl_5$–Et_3SiH	100	71
$TaCl_5$–9BBN[c]	100	70
$TaCl_5$–Ph_4Sn	100	25
$NbCl_5$–n-Bu_4Sn	31	0

[a] Polymerized in toluene at 80°C for 6 h; $[M]_0=0.20$ M, [Cat] = 20 mM, [Cocat] = 40 mM

[b] Methanol-insoluble product. Insoluble in all solvents

[c] 9BBN: 9-borabicyclo[3.3.1]nonane

Table 3 Polymerization of *β*-NPA by various catalysts[a]

Catalyst	Monomer conversion (%)	Polymer yield[b] (%)
$TaCl_5$	100	0
$TaCl_5$–n-Bu_4Sn	75	33
$TaCl_5$–Et_3SiH	90	56
$TaCl_5$–9BBN[c]	94	50
$TaCl_5$–Ph_4Sn	36	25
$NbCl_5$–n-Bu_4Sn	32	0

[a] Polymerized in toluene at 80°C for 6 h; $[M]_0=0.20$ M, [Cat] = 20 mM, [Cocat] = 40 mM

[b] Methanol-insoluble product. Insoluble in all solvents

[c] 9BBN: 9-borabicyclo[3.3.1]nonane

unfortunately, insoluble in any organic solvents. Neither $TaCl_5$ alone nor $NbCl_5$–n-Bu_4Sn produced any methanol-insoluble polymer.

Polymer structure

The elemental analyses of poly(*p*-BzDPA) agreed with the calculated values (see the Experimental section). According to the i.r. and ^{13}C n.m.r. spectra, poly(*p*-BzDPA) contained no C≡C bond (cf. the C≡C bond of the monomer, 2200 cm^{-1} in i.r. and δ 89.3 and 89.0 ppm in ^{13}C n.m.r.). These data are compatible with the alternating double bond structure for the main chain. However, no information on regio- and stereo-specificities was obtained from i.r. and ^{13}C n.m.r. spectra.

The u.v.–visible spectrum of poly(*p*-BzDPA) had two absorption maxima, $\lambda_{max}=370$ and 430 nm ($\varepsilon_{max}=5700$ and 6000 M^{-1} cm^{-1}, respectively), and the absorption cutoff was ~500 nm. This spectrum resembles those of other substituted poly(DPA)s[2,3].

Polymer properties

The present polymers were all yellow solids. Poly(*p*-BzDPA) dissolved completely in toluene, $CHCl_3$, tetrahydrofuran, anisole, 1,4-dioxane, $(CH_2Cl)_2$, methyl benzoate and acetophenone, partly dissolved in *N*,*N*-dimethylformamide, but did not dissolve at all in hexane, cyclohexane, diethyl ether or acetone. These solubility properties differ somewhat from those of poly(*p*-t-BuDPA) and poly(*p*-n-BuDPA). For instance, the *para*-alkyl polymers are soluble in cyclohexane and diethyl ether, and insoluble in 1,4-dioxane, $(CH_2Cl)_2$, methyl benzoate and acetophenone[2]. Thus poly(*p*-BzDPA) is more soluble in polar solvents and less soluble in aliphatic solvents. A free-standing film could be obtained by casting poly(*p*-BzDPA) from toluene solution.

The weight loss of poly(*p*-BzDPA) begins at around 330°C in air (*Figure 3*). The onset temperatures of weight loss for poly(*p*-PhDPA) and poly(*β*-NPA) are 450 and 420°C, respectively. Although these temperatures are lower than that of poly(DPA) (500°C), the present polymers have a relatively high thermal stability compared to other substituted polyacetylenes.

The tensile properties of poly(*p*-BzDPA) measured at 25°C are as follows: Young's modulus $E=1600$ MPa, tensile strength $\sigma_B=35.2$ MPa, elongation at break $\gamma_B=5.1\%$. Thus this polymer is hard and brittle. The γ_B value is between those of poly(*p*-t-BuDPA) (3.4%) and poly(*p*-n-BuDPA) (6.6%), which is attributable to the mobility and flexibility of the *para*-substituent. The glass transition temperature of the polymer was above 200°C according to dynamic viscoelastic measurement.

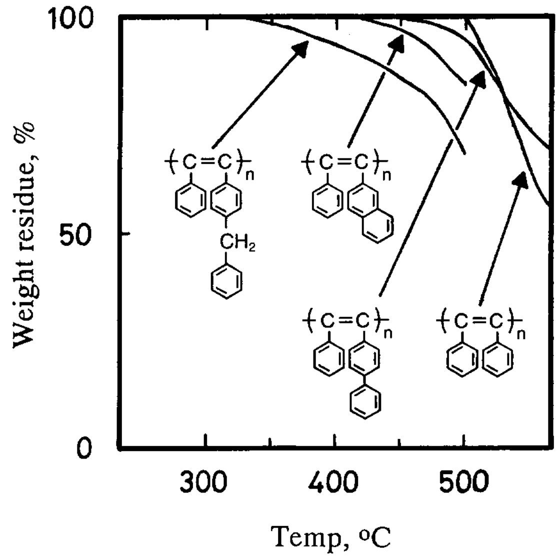

Figure 3 T.g.a. curves of poly(diarylacetylene)s (in air, heating rate 10°C min^{-1})

The oxygen permeability coefficient (P_{O_2}) of poly(*p*-BzDPA) at 25°C is 18 barrers, and the separation factor against nitrogen (P_{O_2}/P_{N_2}) is 2.6. This P_{O_2} value is lower than those of poly(*p*-t-BuDPA) (1100 barrers) and poly(*p*-n-BuDPA) (100 barrers), for which the bulkiness and mobility of the *para*-substituents seem responsible. The permeability coefficients for other gases were as follows (barrer): He, 38; H_2, 63; CO_2, 75; CH_4, 45.

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