Polymer Bulletin 32, 133–140 (1994)

Polymer Bulletin

Synthesis and properties of poly(diphenylacetylenes) having ether linkages

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Summary

Polymerization of 1-phenyl-2-(*p*-phenoxyphenyl)acetylene (*p*-PhODPA), 1-phenyl-2-(*p*-methoxyphenyl)acetylene, and 1-phenyl-2-(*p*-*n*-butoxyphenyl)acetylene was examined. These monomers polymerized with $TaCl_5$–*n*-Bu_4Sn to give methanol-insoluble polymers in over 60% yields. Poly(*p*-PhODPA) was a yellow solid completely soluble in toluene, $CHCl_3$, etc., and its weight-average molecular weight was about 1.0×10^6 or higher. This polymer was thermally very stable (the onset temperature of weight loss in TGA in air was 420 °C). Its oxygen permeability coefficient (P_{O_2}) was 37 barrers (P_{O_2}/P_{N_2} 2.2) and similar to that of natural rubber. In contrast, the other two polymers did not completely dissolve in any organic solvent, and their thermal stability was lower.

Introduction

Diphenylacetylene (DPA) polymerizes in good yields with $TaCl_5$–cocatalyst systems (1). Poly(DPA) exhibits high thermal stability as demonstrated by the onset temperature of weight loss in air being ca. 500 °C. The polymer, however, does not dissolve in any solvents, which restricts its application. Among aliphatic disubstituted acetylenes, symmetrical monomers (e.g., 4-octyne) provide insoluble polymers, whereas unsymmetrical ones (e.g., 2-octyne) yield soluble polymers. In accordance with this tendency, 1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene (*p*-Me_3SiDPA), an unsymmetrical DPA, produces a polymer completely soluble in various organic solvents (2). This polymer has a high weight-average molecular weight ($\overline{M}_w$) over 1×10^6, is thermally appreciably stable, and shows high gas permeability [oxygen permeability coefficient (P_{O_2}) 1100 barrers].

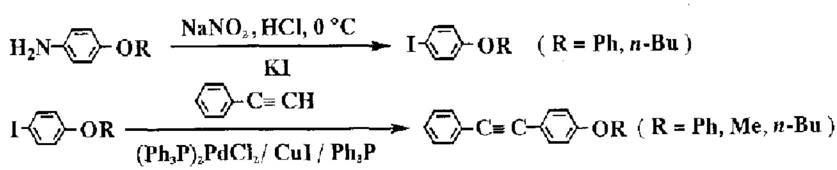
It seems interesting to examine how the polymerization behavior and the polymer properties of DPA will change, when a more polar and somewhat basic phenoxy or alkoxy group is introduced into DPA instead of the less polar trimethylsilyl group.

This study deals with the polymerization and polymer properties of DPAs with a *p*-phenoxy or *p*-alkoxy group. The monomer used are 1-phenyl-2-(*p*-phenoxyphenyl)acetylene (*p*-PhODPA), 1-phenyl-2-(*p*-methoxyphenyl)acetylene (*p*-MeODPA), and 1-phenyl-2-(*p*-*n*-butoxyphenyl)-acetylene (*p*-*n*-BuODPA).

Experimental

Materials

The monomers (new compounds) were synthesized through iodination and ethynylation by applying the literature methods (3, 4):



The crude *p*-PhODPA was purified by recrystallization from a methanol–water mixture; mp 69–70 °C, overall yield 10%, purity >99% (by gas chromatography (GC)). *p*-MeODPA was purified in the same way; mp 56–57 °C, overall yield 75%, purity >99% (GC). *p*-*n*-BuODPA was recrystallized from methanol, and then purified by flush column chromatography (Nacalai Tesque Co., silica gel 60; eluent, toluene : hexane = 1:6); mp 50–52 °C, overall yield 17%, purity >99% (GC).

Transition-metal catalysts and organometallic cocatalysts were used without further purification. Toluene as polymerization solvent was purified by a standard method (5).

Procedures

Unless otherwise specified, polymerizations were carried out under the following conditions: in toluene, 80 °C, 3 h, $[M]_0$ = 0.10 M, [Cat] = 20 mM, [Cocat] = 40 mM. The monomer conversion was determined by GC (Silicone DC 550, 0.5 m, 200 °C). A detailed procedure of polymerization has been described elsewhere (2).

The molecular weights of polymers were determined by gel permeation chromatography (GPC; Shimadzu LC-9A liquid chromatograph, eluent $CHCl_3$, polystyrene calibration). Light scattering (LS) was also employed (Otsuka Electronics SLS-600R photometer; in toluene, 25 °C, λ = 633 nm, angle = 30–90°, four-concentration measurements, c = 2.0×10^{-5}–8.0×10^{-5} g/mL). The refractive index increment (dn/dc) was measured in toluene at 25 °C on an Otsuka Electronics DRM-1020 double beam differential refractometer (λ = 633 nm, three-point measurements, c = 1.7×10^{-3}–5.1×10^{-3}

g/mL). The d*n*/dc value of poly(*p*-PhODPA) was 0.183 mL/g.

IR and UV-visible spectra, and gas permeabilities were measured in the same manner as described before (2). Thermogravimetric analyses (TGA) were carried out with a Shimadzu 30B thermal analyzer (heating rate 10 °C/min).

Results and Discussion

Polymerization of Diphenylacetylenes with Ether Linkages

Table I shows results for the polymerization of *p*-PhODPA by various catalysts. When $TaCl_5$ alone was used as catalyst, *p*-PhODPA was completely consumed, but no methanol-insoluble polymer was obtained. When organometallic cocatalysts (i.e., $n\text{-}Bu_4Sn$, Et_3SiH, and 9-borabicyclo[3.3.1]nonane (9BBN)) that are effective to DPA were added in a twofold excess, the monomer polymerized quantitatively, and polymers were obtained in over 60% yields.

Table I. Polymerization of *p*-PhODPA by Various Catalysts[a]

Catalyst	Monomer convn, %	Polymer[b] Yield,%	$\overline{M}_w/10^3$ [c]	$\overline{M}_n/10^3$ [c]
$TaCl_5$	100	0	–	–
$TaCl_5$–$n\text{-}Bu_4Sn$	100	69	1700(1200[d])	400
$TaCl_5$–Et_3SiH	100	65	890 (580[d])	340
$TaCl_5$–9BBN[e]	100	62	1000 (640[d])	390
$TaCl_5$–Ph_3SiH	2	3	110	41
$TaCl_5$–Ph_4Sn	37	4	410	190
$TaCl_5$–vitride[f]	9	3	34	6.2
$NbCl_5$–$n\text{-}Bu_4Sn$	78	0	–	–
WCl_6–$n\text{-}Bu_4Sn$	50	0	–	–
$MoCl_5$–$n\text{-}Bu_4Sn$	0	0	–	–

[a] Polymerized in toluene at 80 °C for 3 h; $[M]_0$ = 0.10 M, [Cat] = 20 mM, [Cocat] = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC. [d] Determined by light scattering. [e] 9BBN: 9-borabicyclo[3.3.1]nonane. [f] Vitride: sodium bis(2-methoxyethoxy)aluminum hydride.

As expected, poly(p-PhODPA) was completely soluble in various organic solvents. The "apparent" weight-average molecular weights ($\overline{M}_w$) by GPC were 9x10^5–17x10^5. Further, the absolute $\overline{M}_w$ values determined by light scattering were 6x10^5–12x10^5, and about two thirds of the values by GPC. This should be because the present polymer is more rigid than vinyl polymers such as polystyrene, and assumes a more expanded conformation in solution.

The monomer conversions and polymer yields were much lower with Ph_3SiH, Ph_4Sn and sodium bis(2-methoxyethoxy)aluminum hydride (Vitride) as cocatalysts. $NbCl_5$-, WCl_6- and $MoCl_5$-based catalysts produced no methanol-insoluble polymers. These results are similar to the case of DPA (1) and Si-containing DPAs (2).

Polymerization of p-MeODPA and p-n-BuODPA was examined (Table II). These monomers also gave methanol-insoluble polymers with mixtures of $TaCl_5$ and suitable cocatalysts. Both of these polymers, however, were partly insoluble in $CHCl_3$, and the molecular weights of soluble parts were lower than that of poly(p-PhODPA). Other types of catalysts were ineffective also to these monomers.

Table II. Polymerization of p-MeODPA and p-n-BuODPA by Various Catalysts[a]

Catalyst	Monomer convn, %	Polymer		
		Yield,%[b]	$\overline{M}_w/10^3$ [c]	$\overline{M}_n/10^3$ [c]
		p-MeODPA		
$TaCl_5$	98	0	–	–
$TaCl_5$–n-Bu_4Sn	97	65	770	240
$TaCl_5$–Et_3SiH	89	55	370	140
$NbCl_5$–n-Bu_4Sn	69	0	–	–
		p-*n*-BuODPA		
$TaCl_5$	98	0	–	–
$TaCl_5$–n-Bu_4Sn	99	58	540	210
$TaCl_5$–Et_3SiH	77	13	250	94
$NbCl_5$–n-Bu_4Sn	69	0	–	–

[a] Polymerized in toluene at 80 °C for 3 h; $[M]_0$= 0.10 M, [Cat] = 20 mM, [Cocat] = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC; $CHCl_3$-soluble part.

The polymerization of *p*-PhODPA by $TaCl_5$–*n*-Bu_4Sn, which accomplished the highest molecular weight, was studied in more detail.

Under the conditions shown in Figure 1, the polymerization of *p*-PhODPA is completed after 15 min, and then the polymer yield is about 70%. The $\overline{M}_w$ of polymer is hardly dependent on monomer conversion and about $1.5x10^6$.

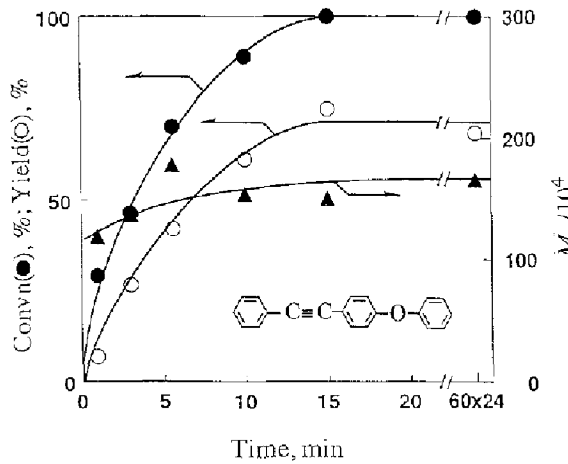


Figure 1. Time profile of the polymerization of *p*-PhODPA by $TaCl_5$–*n*-Bu_4Sn (in toluene, 80 °C, $[M]_0$ = 0.10 M, $[TaCl_5]$ = 20 mM, [*n*-Bu_4Sn] = 40 mM).

To clarify the influence of *p*-phenoxy group on the monomer reactivity, copolymerization of *p*-PhODPA with DPA was carried out with $TaCl_5$–*n*-Bu_4-Sn catalyst in toluene. As seen in Figure 2, *p*-PhODPA is consumed faster than DPA. This seems due to the higher coordination ability of the *p*-phenoxy substituted monomer to the propagating metal carbene.

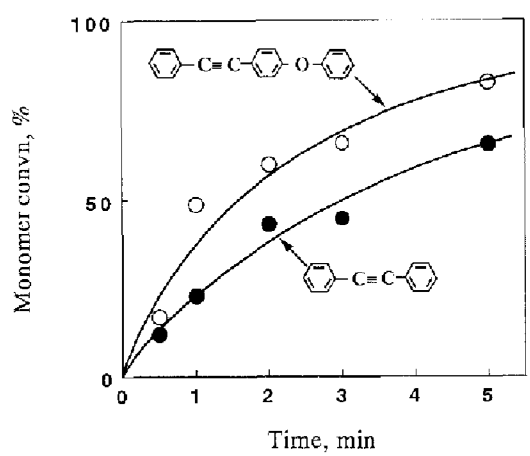


Figure 2. Copolymerization of *p*-PhODPA with DPA by $TaCl_5$–*n*-Bu_4Sn (in toluene, 80 °C, $[M_1]_0$ = $[M_2]_0$ = 0.050 M, $[TaCl_5]$ = 20 mM, [*n*-Bu_4Sn] = 40 mM).

Polymer Structure

The IR spectra of the present polymers showed no absorption due to the C≡C stretching observed around 2200 cm^{-1} in the monomers. Strong absorptions characteristic of asymmetric C–O–C stretchings (ca. 1240 cm^{-1}) were observed in both monomers and polymers.

As seen in Figure 3, poly(*p*-PhODPA) has two absorption maxima [λ_{max} 370 nm (ε_{max} 4100 $M^{-1}cm^{-1}$) and 430 nm (4600)], which extends up to ~500 nm. This spectrum resembles that of poly(*p*-Me_3SiDPA). The soluble parts of both poly(*p*-MeODPA) and poly(*p*-*n*-BuODPA) showed similar absorptions. These spectral data are consistent with the main chain structure composed of alternating double bonds.

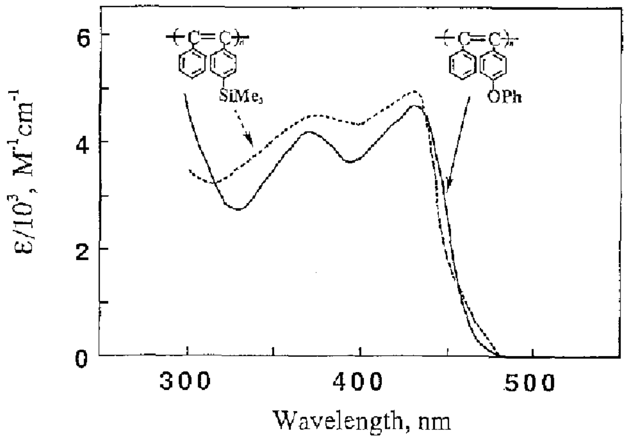


Figure 3. UV-visible spectra of poly(diphenylacetylenes) (measured in THF).

Polymer Properties

Properties of the present polymers were examined by using the samples obtained with $TaCl_5$–*n*-Bu_4Sn under the conditions shown Tables I and II.

Poly(*p*-PhODPA) completely dissolved in benzene, toluene, $CHCl_3$, tetrahydrofuran, anisole, 1,4-dioxane, CH_2Cl_2, $(CH_2Cl)_2$, N,N-dimethylformamide, and methyl benzoate, and partly in CCl_4, dimethyl sulfoxide, and acetophenone, but did not dissolve in hexane, cyclohexane, diethyl ether, ethyl acetate, acetone, methanol, and ethanol. This solubility property fairly differs from that of poly(*p*-Me_3SiDPA) (which is soluble in cyclohexane and diethyl ether, but insoluble in N,N-dimethylformamide and methyl benzoate) (2). Most part of poly(*p*-*n*-BuODPA) dissolved in the good solvents of poly(*p*-PhODPA), while poly(*p*-MeODPA) was less soluble. These findings indicate that introduction of enough bulky substituents is necessary to solubilize poly(DPA). A free-standing film could be obtained by casting poly(*p*-PhODPA) from toluene solution.

The weight loss of poly(*p*-PhODPA) started at 420 °C in air (Figure 4). This temperature is lower than that of poly(DPA) (~500 °C), but fairly high among those of various substituted polyacetylenes. The temperatures for poly-(*p*-MeODPA) and poly-(*p*-*n*-BuODPA) were 310 and 220 °C, respectively, lower than that of poly-(*p*-PhODPA).

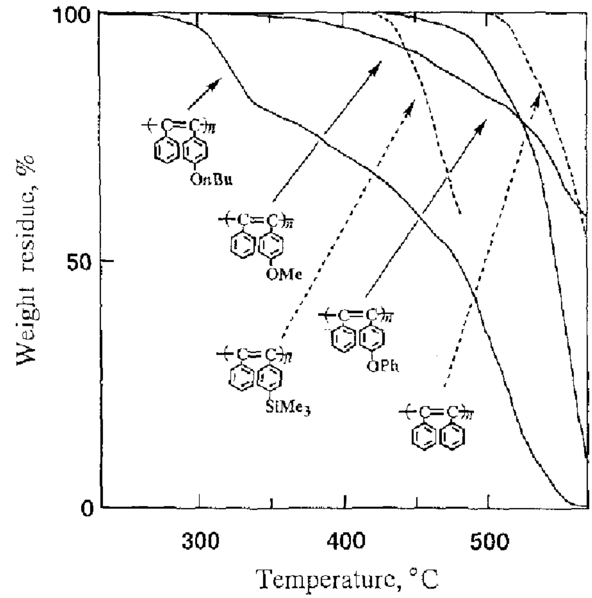


Figure 4. TGA curves of poly(diphenylacetylenes) (heating rate 10 °C/min, in air).

The tensile properties of poly(*p*-PhODPA) measured at 20 °C are as follows: Young's modulus (E) = 2130 MPa, tensile strength (σ_B) = 18.7 MPa, elongation at break (γ_B) = 0.86%. Thus, this polymer is harder and more brittle than poly(*p*-Me_3SiDPA) (E = 1460 MPa, σ_B = 19 MPa, γ_B = 1.5% at 25 °C). The glass transition temperature of poly(*p*-PhODPA) was above 200 °C according to the dynamic viscoelastic measurement.

The oxygen permeability coefficient (P_{O_2}) of poly(*p*-PhODPA) at 25 °C was 37 barrers (P_{O_2}/P_{N_2} 2.2), close to that of natural rubber (23 barrers). The permeability coefficients for other gases were as follows: H_2 106, He 71, CH_4 28, and CO_2 58 barrers.

Acknowledgement

We thank Dr. Y. Chujo (Department of Polymer Chemistry, Kyoto University) for TGA analyses.

References

1. A. Niki, T. Masuda, and T. Higashimura, *J. Polym. Sci., Part A: Polym. Chem.*, **25**, 1533 (1987).
2. K. Tsuchihara, T. Masuda, and T. Higashimura, *Macromolecules*, **25**, 5816 (1992).
3. H. J. Lucus and E. R. Kennedy, *Org. Syn.*, Coll. Vol. **1**, 2nd ed., p. 144 (1961).
4. K. Sonogashira, Y. Sohda, and N. Hagihara, *Tetrahedron Lett.*, **93**, 253 (1975).
5. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, Oxford, 1980.

Accepted January 5, 1994 S