Polymerization of 1-(1-Naphthyl)-1-propyne by Nb and Ta Catalysts and Polymer Properties: Effects of the 1-Naphthyl Group

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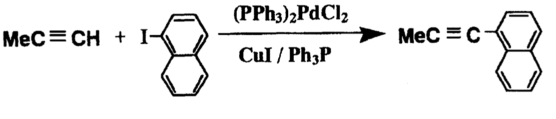
1-(1-Naphthyl)-1-propyne polymerized in the presence of $NbCl_5$–cocatalyst systems to give virtually selectively a new polymer $\overline{M}_w$ ca.3×10^5) in high yields. Catalysts based on $TaCl_5$ produced mixtures of the polymer and cyclotrimers. The polymer was a pale-yellow solid soluble in various organic solvents (e.g., toluene, $CHCl_3$), and formed a free-standing film on solution casting. The onset temperature of the weight loss of the polymer in air was ca. 340 °C, which is higher than that (280 °C) of poly(1-phenyl-1-propyne) [poly(1-PP)]. The oxygen permeability coefficient at 25 °C was 80 barrers and one order of magnitude higher than that of poly(1-PP). These results are explicable in terms of the steric effects of the 1-naphthyl group.

Disubstituted acetylenes are known to polymerize with Nb and Ta catalysts. Among them, 1-phenyl-1-propyne[1,2] (MeC≡CPh; 1-PP) forms a polymer having a weight-average molecular weight ($\overline{M}_w$) of over 1×10^6. The polymer is a white solid which is soluble in various organic solvents. This polymer is thermally fairly stable, as is seen from its onset temperature of the weight loss in air (T_0) being 280 °C. Its gas permeability is rather low among those of various substituted polyacetylenes.[3] It seems to be interesting to examine how the polymerization behavior and polymer properties would change if the phenyl group of a monomer were to be replaced by the bulky 1-naphthyl group.

The present paper deals with the polymerization of 1-(1-naphthyl)-1-propyne (1-NP) and properties of the product polymer (Chart 1). 1-NP polymerized with $NbCl_5$-based catalysts to give a new, high-molecular-weight polymer in excellent yields. The polymer showed a higher thermal stability and a higher gas permeability than does poly(1-PP).

Experimental

Materials. The monomer (new compound) was prepared according to Eq. 1.



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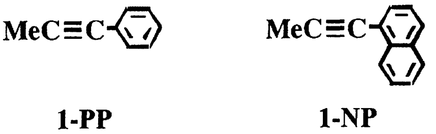

1-PP **1-NP**

Chart 1.

1-(1-Naphthyl)-1-propyne: After being flushed with dry nitrogen, a 500-ml flask was charged with Et_3N (250 ml), $(Ph_3P)_2PdCl_2$ (1.4 g, 2.0 mmol), Ph_3P (2.1 g, 7.9 mmol), CuI (2.3 g, 11.8 mmol), and 1-iodonaphthalene (28.7 ml, 0.20 mol). Then, propyne (22.4 ml, 0.39 mol) was bubbled for 5 min into the mixture at −10°C, and the mixture was stirred for an additional 1 h at room temperature. After the completion of the reaction was confirmed by gas chromatography (GC), the Et_3N was evaporated. Et_2O (300 ml) was then added, and insoluble salts were filtered off. The solution was washed with 5% HCl and water. The organic phase was dried over anhydrous Na_2SO_4 overnight, and the Et_2O was evaporated. The product was distilled at reduced pressure; bp 100—101 °C/4 mmHg (1 mmHg=133.322 Pa), yield 84%, purity >99.9% (GC), d_4^{20} 1.008. IR (KBr) 3060 (s), 2955 (m), 2914 (s), 2219 (m, $\nu_{C\equiv C}$), 1586 (s), 1437 (m), 1397 (s), 1375 (m), 1017 (s), 799 (s), and 774 (s), cm^{-1}. ^1H NMR ($CDCl_3$) δ=7.8—7.2 (naphthyl) and 2.1 (s, 3, Me). ^{13}C NMR ($CDCl_3$) δ=133.4, 133.1, 129.9, 128.1, 127.8, 126.3, 126.2, 126.1, 125.1, 121.7, 90.7, (MeC≡), 77.8 (≡CNp), and 4.4.

Transition-metal chlorides and organometallic cocatalysts were all commercially obtained and used without further purification. Polymerization solvents were purified by the standard methods.[4]

Procedures. Polymerizations were carried out as described elsewhere.[2] Monomer conversions were determined by GC. The molecular weights of the polymers were determined by gel permeation chromatography (GPC; eluent, $CHCl_3$, polystyrene calibration) and by laser-light scattering (in toluene, λ=633 nm; angles=30—110 °C; four-concentration measurements; $c=6.3\times10^{-3}$—2.5×10^{-4} g ml^{-1}). The refractive index increment (dn/dc) value of poly(1-NP) was 0.184 ml g^{-1}.

Measurements of the IR, NMR, and UV-visible spectra, thermogravimetric analysis (TGA), gas permeation, etc. were carried out in the same manner as described before.[5)] The analytical and spectral data of the polymer (sample: Table 1, $NbCl_5$–*n*-Bu_4Sn) are as follows: Calcd for $(C_{13}H_{10})_n$: C, 93.92; H, 6.08 %. Found: C, 93.35; H, 6.03%. IR (KBr) 2855 (s), 2718 (s), 2413 (m), 1806 (m), 1727 (m), 1622 (m), 1592 (m), 1576 (m), 1441 (s), 1368 (s), 1084 (s), and 858 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ=8.3—5.8 (olefinic, naphthyl) and 2.6—1.7 (Me). ^{13}C NMR ($CDCl_3$) δ=150—115 (olefinic, naphthyl) and 27—17 (Me).

Results and Discussion

Polymerization by Nb and Ta Catalysts. As can be seen in Table 1, a polymer was obtained in good yield even with $NbCl_5$ alone. Polymer degradation, however, occurred in this system, as shown below. When *n*-Bu_4Sn, Ph_4Sn, and Et_3SiH were used as cocatalysts, polymers were quantitatively obtained. These results are similar to those of 1-PP.[2)] The formed polymers dissolved in toluene and $CHCl_3$. The absolute $\overline{M}_w$ values determined by light scattering reached 24×10^4—35×10^4. The relative $\overline{M}_w$ by GPC versus polystyrene standards were 18×10^4—26×10^4, smaller than the values by light scattering. This should be because the present polymer takes a less expanded conformation than dose polystyrene, due to the high molecular weight of the repeat unit and/or the large difference in the bulkiness of the two pendant groups. Since the $\overline{M}_w$ values determined by GPC and light scattering were, however, not very different, a more facile GPC method was employed in additional experiments (cf. Figs. 1, 2, and 3 and Table 2).

When $TaCl_5$-based catalysts were used, although the monomer conversions were high, the yields of methanol-insoluble polymer were much lower than those with the $NbCl_5$-based counterparts (Table 1). Such tendencies have also been observed in the polymerization of 1-phenyl-1-alkynes and internal alkynes,[1,5)] whereas diphenylacetylenes polymerize with $TaCl_5$-based catalyst and not with those based on $NbCl_5$.[6,7)] The methanol-soluble products are thought to be cyclotrimers (mixtures of 1,3,5- and 1,2,4-isomers) according to a single GPC peak and ^1H NMR data [δ=8.4—6.8 (aromatic), δ=2.4—1.2 (methyl)].

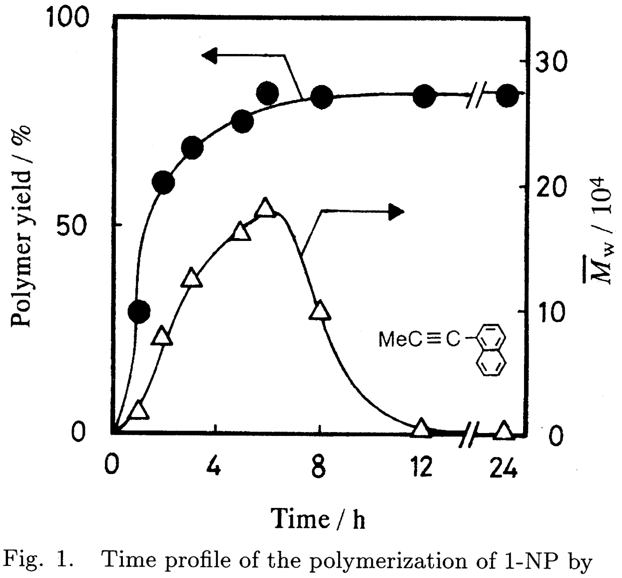

Fig. 1. Time profile of the polymerization of 1-NP by $NbCl_5$ (in toluene, 80 °C, $[M]_0$=0.50 M, $[NbCl_5]$=10 mM; $\overline{M}_w$ by GPC).

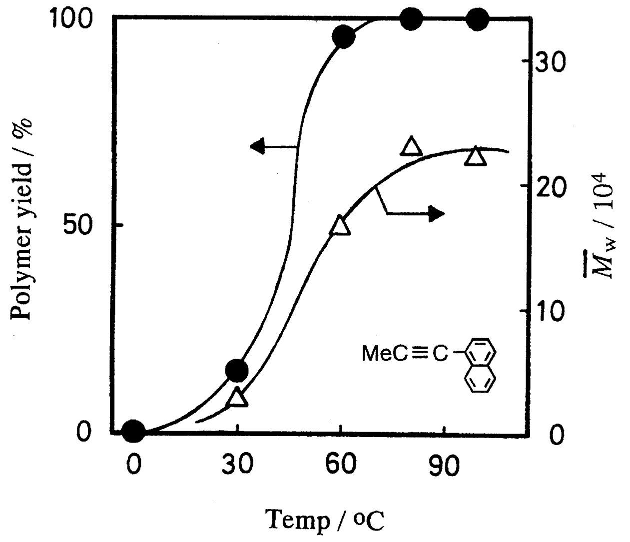

Fig. 2. Effect of temperature on the polymerization of 1-NP by $NbCl_5$–*n*-Bu_4Sn (in toluene, 6 h, $[M]_0$=0.50 M, $[NbCl_5]$=10 mM, [*n*-Bu_4Sn]=20 mM; $\overline{M}_w$ by GPC).

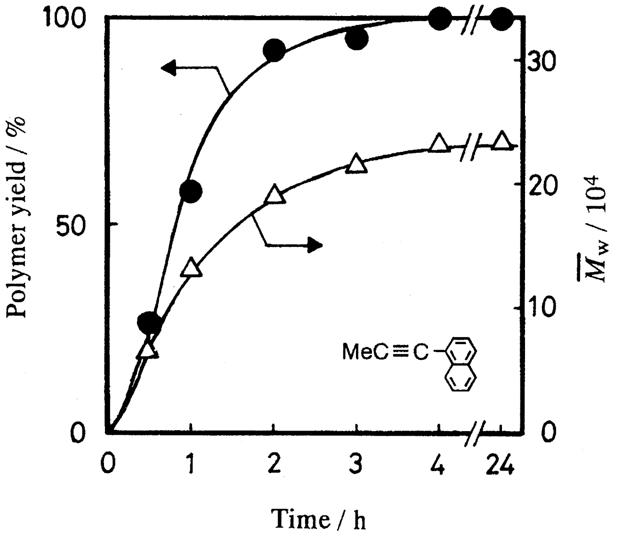

Fig. 3. Time profile of the polymerization of 1-NP by $NbCl_5$–*n*-Bu_4Sn (in toluene, 80 °C, $[M]_0$=0.50 M, $[NbCl_5]$=10 mM, [*n*-Bu_4Sn]=20 mM; $\overline{M}_w$ by GPC).

Though 1-PP polymerizes in good yields with $NbCl_5$ or $TaCl_5$ alone, the molecular weight of the polymer decreases after complete consumption of the monomer.[1)] It was thus examined how the naphthyl group would affect this phenomenon. The monomer conversion reached 100% with $NbCl_5$ alone after 6 h, and the polymer was obtained in over 80% yields (Fig. 1). The $\overline{M}_w$ of the polymer was 18×10^4 at that time; thereafter, the

Table 1. Polymerization of 1-NP by Various Catalysts[a]

Cocatalyst	Monomer convn/%	Polymer[b] Yield/%	$\bar{M}_w/10^3$ LS[c]	$\bar{M}_w/10^3$ GPC	$\bar{M}_n/10^3$ GPC
		$NbCl_5$–cocatalyst			
None	100	82	250	180	100
n-Bu_4Sn	100	100	300	230	100
Ph_4Sn	100	100	240	200	110
Et_3SiH	100	100	350	260	130
Ph_3SiH	100	93	—	11	4.5
Ph_3Sb	100	99	—	22	8.4
Ph_3Bi	100	96	—	78	51
		$TaCl_5$–cocatalyst			
None	100	27	—	26	17
n-Bu_4Sn	95	15	—	69	42
Ph_4Sn	100	23	—	230	110
Et_3SiH	100	18	—	110	67
Ph_3SiH	92	29	—	140	74
Ph_3Sb	24	15	—	220	89
Ph_3Bi	93	25	—	300	110

a) Polymerized in toluene at 80 °C for 6 h; $[M]_0=0.50$ M, [Cat]=10 mM, [Cocat]=20 mM. b) Methanol-insoluble product. c) Light scattering.

Table 2. Solvent Effects on the Polymerization of 1-NP by $NbCl_5$–n-Bu_4Sn (1 : 2)[a]

Solvent	Monomer convn/%	Polymer[b] Yield/%	$\bar{M}_w/10^{3c)}$	$\bar{M}_n/10^{3c)}$
Toluene	100	100	230	100
Heptane	67	63	220	110
PhOMe	100	81	140	73
CCl_4	65	58	51	22
$(CH_2Cl)_2$	100	86	57	25

a) Polymerized at 80 °C for 6 h; $[M]_0=0.50$ M, $[NbCl_5]=10$ mM, $[n\text{-}Bu_4Sn]=20$ mM. b) Methanol-insoluble product. c) Determined by GPC.

$\bar{M}_w$ sharply decreased to become no more than several thousand after 24 h. Thus, despite the presence of bulky 1-naphthyl groups, poly(1-NP) suffers degradation during polymerization like poly(1-PP).

Polymerization by $NbCl_5$–n-Bu_4Sn (1 : 2). The polymerization of 1-NP was studied in more detail by using the $NbCl_5$–n-Bu_4Sn (1 : 2) catalyst, which proved to provide a high-molecular-weight polymer.

Solvent effects on the polymerization were studied (Table 2). High-molecular-weight polymers were obtained in good yields not only in the hydrocarbon-based solvents (toluene, heptane), but also in anisole. Though the polymerization also proceeded in chlorine-containing solvents [CCl_4 and $(CH_2Cl)_2$], the molecular weights of the polymers were lower. Regarding the polymerization temperature, polymers were obtained at 30 °C and above (Fig. 2). Both the yield and the molecular weight of the polymer increased with increasing temperature to reach 100% and ca. 25×10^4 (GPC), respectively, at 80—100 °C.

Under the conditions given in Fig. 3, the polymerization of 1-NP was completed in 4 h to give a methanol-insoluble polymer quantitatively. The reaction was slower than that of 1-PP, which is consumed within 30 min under the same conditions. The $\bar{M}_w$ of the polymer increased approximately in proportion to the polymer yield to finally reach 23×10^4. This is indicative of the presence of a long-lived propagating species. Such tendencies have also been observed in the polymerization of 1-phenyl-1-alkynes by $NbCl_5$ and $TaCl_5$ catalysts.[1] The polymer molecular weights did not decrease, even though the polymerization systems were left for over 24 h, indicating that no polymer degradation occurred in the presence of n-Bu_4Sn as a cocatalyst (cf. Fig. 1). It has been confirmed in the polymerization of 1-PP that not only n-Bu_4Sn, but also the other cocatalysts as shown in Table 1, are effective in prohibiting polymer degradation.[2] A possible reason for this phenomenon is that a moiety of the cocatalysts is present as a ligand of the propagating species to sterically prevent polymer degradation due to secondary metathesis.

To clarify the influence of the 1-naphthyl group on the reactivity, copolymerization of 1-NP with 1-PP was carried out with the $NbCl_5$–n-Bu_4Sn catalyst in toluene. As can be seen in Fig. 4, 1-PP was consumed faster than 1-NP. This seems to be due to the steric effect of the 1-naphthyl group.

Polymer Structure. The analytical values of poly(1-NP) agreed well with the calulated values (see the Experimental). The IR spectrum showed no absorption due to the C≡C stretching observed at 2200 cm^{-1} in the monomer. Absorption due to C=C stretching was observed at around 1650 cm^{-1} as a shoulder. The ^1H NMR spectrum exhibited signals due to the olefinic

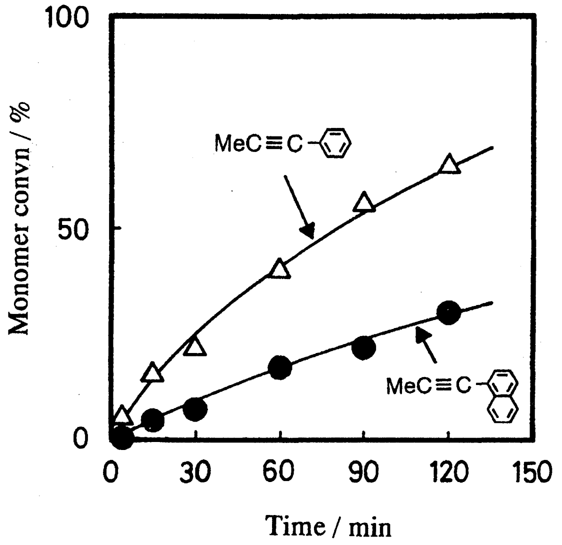

Fig. 4. Copolymerization of 1-NP with 1-PP by NbCl-n-Bu$_4$Sn (in toluene, 80 °C, $[M_1]_0=[M_2]_0=0.25$ M, $[NbCl_5]=10$ mM, $[n\text{-}Bu_4Sn]=20$ mM).

and aromatic protons (δ=8.3—5.8) as well as the methyl protons (δ=2.6—1.7), but no other unidentifiable signals. The ^{13}C NMR spectrum of the monomer showed two peaks due to the acetylenic carbons at δ=90.7 and 77.8, which disappeared in the polymer. Signals due to the sp^2 carbons of the main chain and the 1-naphthyl group (δ=150—115) and those of methylene carbons (δ=27—17) were observed in the polymer.

As can be seen in Fig. 5, poly(1-NP) showed an absorption maximum (ε_{max} 3700 M^{-1} cm^{-1}) at 290 nm in the UV-visible spectrum, which is similar to that of poly(1-PP). The cutoff wavelength is ca. 420 nm, which is slightly longer than that of poly(1-PP). These spectral data are consistent with a main-chain structure comprising alternating double bonds.

General Properties of the Polymer. The present polymer is a pale-yellow solid (cf. poly(1-PP) colorless). It completely dissolved in toluene, CCl$_4$, CHCl$_3$, (CH$_2$Cl)$_2$, tetrahydrofuran, 1,4-dioxane, anisole, methyl benzoate, and acetophenone; partly dissolved in *N,N*-dimethylformamide; but did not dissolve at all in hexane, cyclohexane, diethyl ether, and acetone. These solubility properties are practically the same as those of poly(1-PP). However, although poly(1-PP) is soluble in cyclohexane, the present polymer is not. A free-standing film could be fabricated by casting poly(1-NP) from a toluene solution.

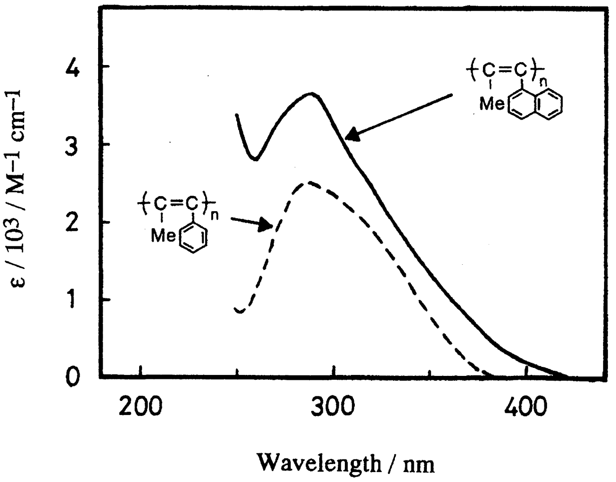

Fig. 5. UV-visible spectra of poly(1-aryl-1-propyne)s (measured in tetrahydrofuran).

The onset temperature of the weight loss in air for poly(1-NP) is 340 °C, whereas that for poly(1-PP) is 280 °C (Fig. 6). Thus, the introduction of a naphthyl group in place of the phenyl group of 1-PP considerably improves the thermal stability. The mechanical and thermal properties of poly(1-NP) along with those of poly(1-PP) are summarized in Table 3. According to tensile tests at 25 °C, the present polymer is even less ductile than poly(1-PP), which is due to the naphthyl group. The glass transition temperature was higher than 200 °C according to a dynamic viscoelastic measurement.

Gas Permeability of the Polymer. The oxy-

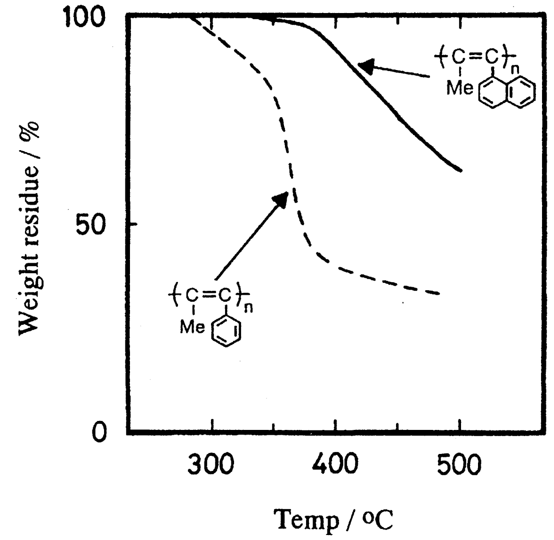

Fig. 6. TGA curves of poly(1-aryl-1-propyne)s (in air, heating rate 10 °C min^{-1}).

Table 3. Mechanical and Thermal Properties of Poly(1-aryl-1-propyne)s[a]

	Poly(1-NP)	Poly(1-PP)[b]
Young's modulus/MPa	1700	2500
Tensile strength/MPa	39	93
Elongation at break/%	2.6	4.3
T_g[c]/°C	>200	ca. 200
T_s[d]/°C	338	272

a) Tensile properties were examined at 25 °C. b) Data from Ref. 1. c) Glass transition temperatures (T_g) were estimated by dynamic viscoelasticity. d) Softening temperature.

Table 4. Gas Permeability of Poly(1-aryl-1-propyne)s

Polymer	P[a)]						
	He	H_2	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}
Poly(1-NP)	110	220	80	26	250	24	3.1
Poly(1-PP)[b)]	30	43	6.3	2.2	25	2.8	2.9

a) Gas permeability coefficients at 25 °C in the units of 1×10^{-10} cm^3 (STP)cm/(cm^2 · s · cm Hg) (=1 barrer).
b) Data from Ref. 3.

gen permeability coefficient (P_{O_2}) of poly(1-NP) is 80 barrers (Table 4), ca. 12-times as large as that of poly(1-PP). It is thus noteworthy that the replacement of phenyl by 1-naphthyl results in a considerable enhancement of P_{O_2}. The P_{O_2} value of the present polymer is three-times larger than that of natural rubber (23 barrers), and is fairly large among those of various substituted polyacetylenes.3) The separation factor between oxygen and nitrogen (P_{O_2}/P_{N_2}) is 3.1. It is noted that poly(1-NP) is 3—13 times more permeable than is poly(1-PP) to any gas.

Comparison with 1-PP. i) In the polymerization of 1-NP by $NbCl_5$ and $TaCl_5$ alone, the molecular weight of the polymer decreases after the monomer has been completely consumed. In contrast, polymer degradation is suppressed when n-Bu_4Sn is added as a cocatalyst. These are the same tendencies as for 1-PP. ii) The $\overline{M}_w$ of the poly(1-NP) obtained with $NbCl_5$–n-Bu_4Sn is 23×10^4 according to GPC, which is somewhat lower than that (37×10^4) of poly(1-PP). This seems to be due to the weaker coordinating ability of the monomer to the propagating species, which is attributable to the steric effect of the 1-naphthyl group. iii) Despite the presence of bulky naphthyl groups, the present polymer is soluble in various organic solvents, as is poly(1-PP). Further, poly(1-NP) is thermally more stable than poly(1-PP). This is explained in terms of the fact that bulky naphthyl groups protect the main chain from oxidative degradation. iv) Poly(1-PP) is one of the substituted polyacetylenes that show the lowest gas permeability.3) The oxygen permeability coefficient of poly(1-NP) is one order of magnitude larger than that of poly(1-PP). This suggests that sterically crowded poly(1-NP) has more molecular-scale voids that does poly(1-PP).

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