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Polymerization of propynes bearing diphenylamino or indolyl groups

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Summary

Nitrogen-containing acetylenic monomers including 3-(*N*,*N*-diphenylamino)-1-propyne (DPAP), *N*-(2-propynyl)indole (PI), 2-methyl-*N*-propynyl)indole (2-MePI) and 3-methyl-*N*-(2-propynyl)indole (3-MePI) polymerized in the presence of various transition metal catalysts. Poly(DPAP) was obtained with WCl_6, $MoCl_5$, Rh and Fe catalysts, and its weight-average molecular weights (M_w) reached $140x10^3$. Polymerization of PI and 2-MePI by Rh and Fe catalysts gave good yields of high molecular weight polymers with M_w of $340x10^3$ and $640x10^3$, respectively. Polymerization of 3-MePI by WCl_6- and $MoCl_5$-based catalysts resulted in a soluble polymer ($M_w = 52x10^3$), whereas the use of Rh and Fe catalysts led to the formation of an insoluble polymer. All the polymers exhibited cutoff wavelengths around 450-500 nm, meaning the moderate to fair conjugation along the polymer backbones.

Introduction

Substituted polyacetylenes have been known to exhibit characteristic properties based on the conjugation through alternating double bonds of the main chains [1]. They are potentially useful in areas of nonlinear optics, photo- and electroluminescent materials, organic conductors and so on. However, most substituted polyacetylenes have twisted main chains due to the repulsion between pendants, which reduces the degree of conjugation along the main chain. Therefore, many polyacetylenes with bulky pendant groups are generally colorless or only slightly colored, and show quite low unpaired-electron densities.

One of the approaches to enhance the optical and electrical properties of polymers is represented by the introduction of nitrogen-containing aromatic pendants such as carbazolyl group to the polymer backbones [2]. This idea has been applied to polyacetylenes, and several polymers from substituted acetylenes containing carbazolyl groups have been prepared [3]. We have also reported the polymerization of carbazole-containing acetylenes including *N*-ethynylcarbazole (ECz) [3b] and 1-(4-*N*-carbazolylpheny)-2-phenylacetylene (CzDPA) [3c] (Chart). It was demonstrated that poly(ECz) and poly(CzDPA) show characteristic properties as nonlinear optical and photoconductive materials, respectively.

As a part of our studies on the synthesis of the polymers from nitrogen-containing acetylenes, attempts have been made to polymerize *N*-(2-propynyl)carbazole (PCz) [3d]. Although good yield of poly(PCz) was attainable with W or Mo catalysts, extremely poor solubility of poly(PCz) inhibited detailed investigation on their properties [4]. On the basis of these backgrounds, we report here the polymerization of various counterparts of PCz for the purpose of synthesizing nitrogen-containing polyacetylenes with excellent solubilities and satisfactory molecular weights.

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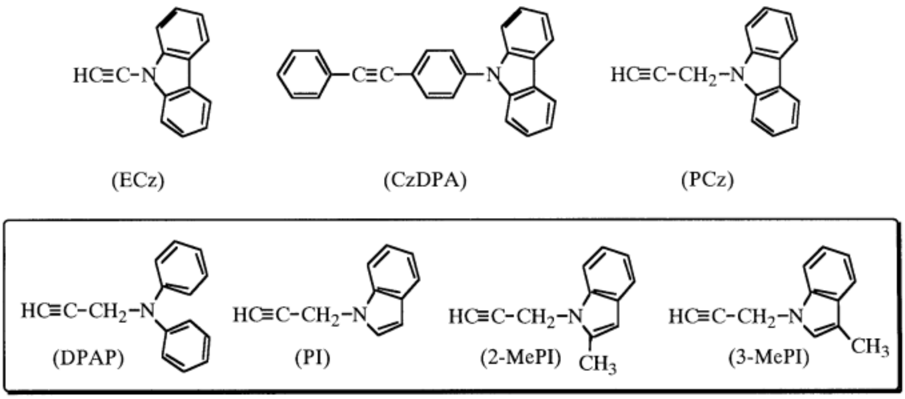

Chart

Results and discussion

The monomers employed in the present study are 3-(*N*,*N*-diphenylamino)-1-propyne (DPAP), *N*-(2-propynyl)indole (PI), 2-methy-*N*-(2-propynyl)indole (2-MePI) and 3-methyl-*N*-(2-propynyl)indole (3-MePI) (Chart). They were readily prepared by the reaction of propargyl bromide with diphenylamine or corresponding indoles in the presence of NaH in DMSO [3c]. Polymerizations were carried out by using transition metal catalysts in toluene, and the results for the polymerization of these monomers are summarized in Table 1.

DPAP polymerized with various transition-metal catalysts such as W, Mo, Rh, and Fe catalysts (runs 1-5). Especially, a polymerization run using $[Rh(nbd)Cl]_2$ at 0°C gave the polymer with highest molecular weight (run 4). In the cases of W and Mo catalysts, no polymers were obtained when the polymerization was conducted without cocatalyst. Poly(DPAP)s obtained with W, Mo and Rh catalysts were soluble in organic solvents such as toluene, chloroform, THF and 1,4-dioxane. In contrast, Fe(acac)-Et_3Al gave a polymer which was only partly soluble in common solvents. This is probably due to the difference in the steric structure of the main chain, because Fe catalysts tend to provide cis-cisoidal polyacetylenes which often show very poor solubility [1b].

In contrast to DPAP, neither of PI and 2-MePI polymerized with W and Mo catalysts (runs 6, 7, 11 and 12). Formation of polymers from 3-MePI by these catalysts (runs 16 and 17) suggests that the reduced steric hindrance around nitrogen atom in PI and the enhanced basicity of nitrogen atom due to the 2-Me group in 2-MePI led to the deactivation of the catalysts. Rh and Fe catalysts were active for the polymerization of all these indole-containing monomers, giving polymers in good yields (runs 8-10, 13-15, 18 and 19). It is worthy to note that very high molecular weight polymers were obtained from PI and 2-MePI. For example, the highest weight-average molecular weight (M_w) of poly(2-MePI) was as high as $640x10^3$ (run 15). High molecular weight poly(2-MePI) was also obtainable with Rh catalyst by increasing the monomer concentration (runs 13 and 14). In the case of PI, polymerization at low temperature achieved the highest molecular weight ($M_w = 340x10^3$). Poly(PI) and poly(2-MePI) showed good solubilities in common solvents irrespective of the kind of catalysts, whereas the poly(3-MePI) formed with Rh and Fe catalysts were insoluble.

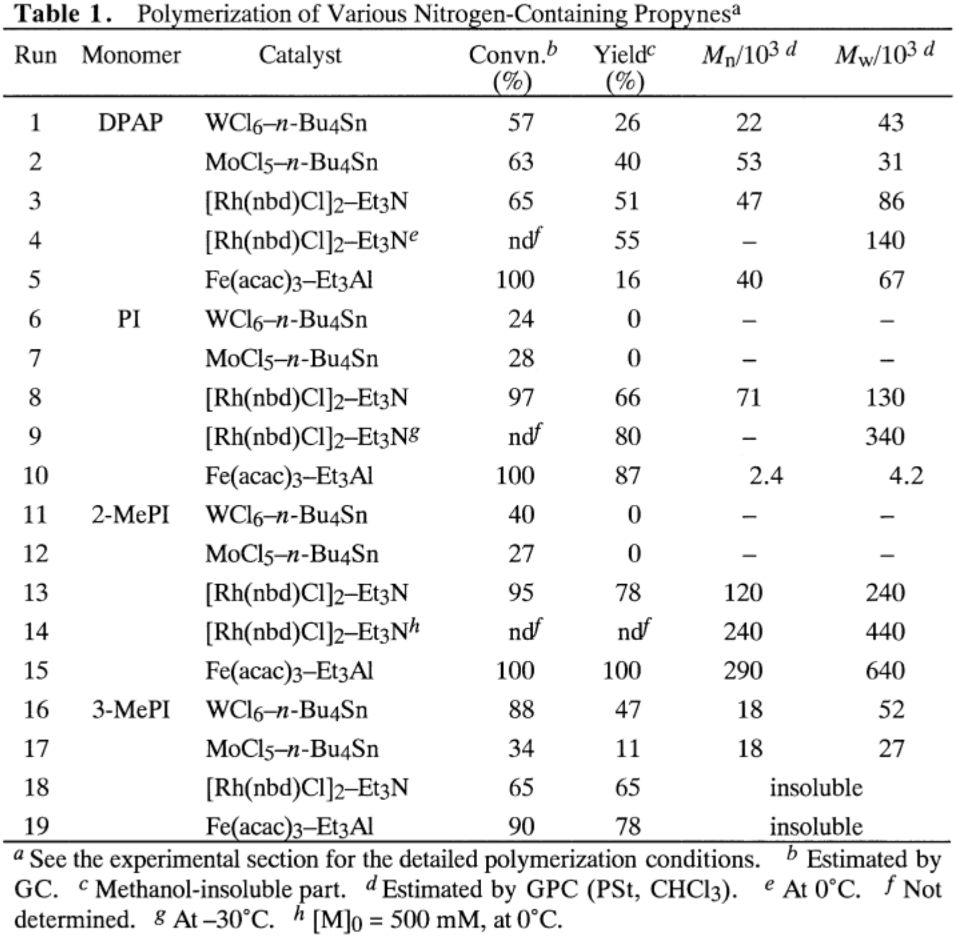

Table 1. Polymerization of Various Nitrogen-Containing Propynes[a]

Run	Monomer	Catalyst	Convn.[b] (%)	Yield[c] (%)	$M_n/10^3$ [d]	$M_w/10^3$ [d]
1	DPAP	$\mathrm{WCl_6}$–n-$\mathrm{Bu_4Sn}$	57	26	22	43
2		$\mathrm{MoCl_5}$–n-$\mathrm{Bu_4Sn}$	63	40	53	31
3		$\mathrm{[Rh(nbd)Cl]_2}$–$\mathrm{Et_3N}$	65	51	47	86
4		$\mathrm{[Rh(nbd)Cl]_2}$–$\mathrm{Et_3N}$[e]	nd[f]	55	–	140
5		$\mathrm{Fe(acac)_3}$–$\mathrm{Et_3Al}$	100	16	40	67
6	PI	$\mathrm{WCl_6}$–n-$\mathrm{Bu_4Sn}$	24	0	–	–
7		$\mathrm{MoCl_5}$–n-$\mathrm{Bu_4Sn}$	28	0	–	–
8		$\mathrm{[Rh(nbd)Cl]_2}$–$\mathrm{Et_3N}$	97	66	71	130
9		$\mathrm{[Rh(nbd)Cl]_2}$–$\mathrm{Et_3N}$[g]	nd[f]	80	–	340
10		$\mathrm{Fe(acac)_3}$–$\mathrm{Et_3Al}$	100	87	2.4	4.2
11	2-MePI	$\mathrm{WCl_6}$–n-$\mathrm{Bu_4Sn}$	40	0	–	–
12		$\mathrm{MoCl_5}$–n-$\mathrm{Bu_4Sn}$	27	0	–	–
13		$\mathrm{[Rh(nbd)Cl]_2}$–$\mathrm{Et_3N}$	95	78	120	240
14		$\mathrm{[Rh(nbd)Cl]_2}$–$\mathrm{Et_3N}$[h]	nd[f]	nd[f]	240	440
15		$\mathrm{Fe(acac)_3}$–$\mathrm{Et_3Al}$	100	100	290	640
16	3-MePI	$\mathrm{WCl_6}$–n-$\mathrm{Bu_4Sn}$	88	47	18	52
17		$\mathrm{MoCl_5}$–n-$\mathrm{Bu_4Sn}$	34	11	18	27
18		$\mathrm{[Rh(nbd)Cl]_2}$–$\mathrm{Et_3N}$	65	65	insoluble	
19		$\mathrm{Fe(acac)_3}$–$\mathrm{Et_3Al}$	90	78	insoluble	

[a] See the experimental section for the detailed polymerization conditions. [b] Estimated by GC. [c] Methanol-insoluble part. [d] Estimated by GPC (PSt, $\mathrm{CHCl_3}$). [e] At 0°C. [f] Not determined. [g] At –30°C. [h] $[\mathrm{M}]_0$ = 500 mM, at 0°C.

Figure 1 shows thermogravimetric analysis (TGA) curves measured in air for the polymers produced by $\mathrm{[Rh(nbd)Cl]_2}$-$\mathrm{Et_3N}$. All of the polymers started weight loss in the range of 200-300°C. Although poly(DPAP) was less thermally stable, other polymers showed moderate thermal stabilities which are comparable to that of poly(phenylacetylene) [poly(PA)]. In other words, introduction of indolyl groups does not reduce the thermal stability of polyacetylenes. Furthermore, the present polymers did not undergo autooxidation under aerobic conditions at room temperature, while aliphatic polymers from terminal acetylenes are rapidly oxidized in air to lead to the degradation of polymer backbones [5].

In general, polymers from aliphatic terminal acetylenes are colorless and show no absorption in the visible region. On the contrary, the present polymers were yellow or pale yellow and exhibited absorption bands in the visible region (Figure 2). In addition to the absorptions due to the phenyl and indolyl groups at 280-300 nm, all the resulting polymers showed absorption bands in the range of 330-500 nm. Introduction of a methyl group to the indolyl group seems to cause a red-shift of the absorption of the polymers. Namely, the cutoff wavelengths of poly(2-MePI) and poly(3-MePI) were slightly longer than that of poly(PI).

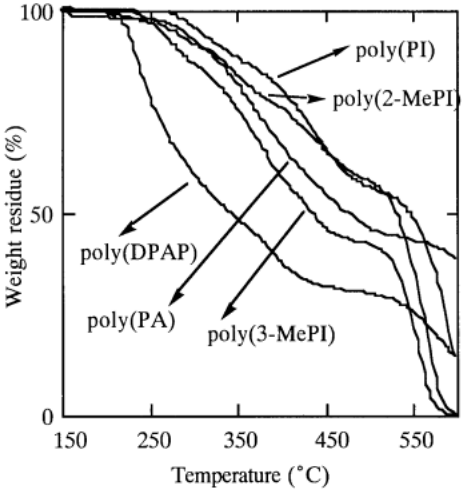

Figure 1. TGA curves of the present polymers and poly(PA) (in air, 10°C/min).

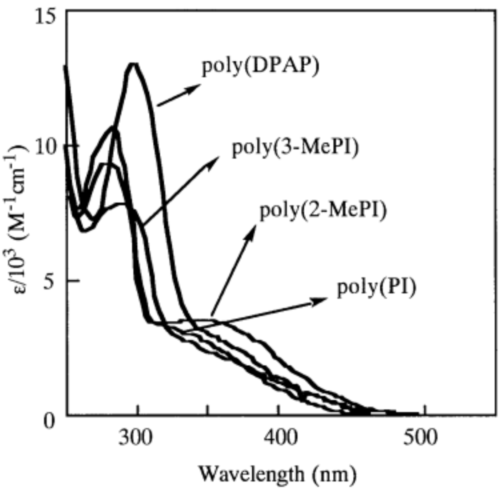

Figure 2. UV-vis. spectra of the present polymers (in $CHCl_3$).

In summary, we have demonstrated the synthesis of polyacetylenes having dimethylamino or indolyl groups as side chains. Apart from the insolubility of the carbazole-bearing counterpart, poly(PCz), the present polymers exhibited excellent solubilities and satisfactory molecular weights. Investigation of the functions of the present polymers as well as the synthesis of related polymers is now ongoing.

Experimental

Materials. All the solvents used were distilled by the standard procedures. $MoCl_5$, WCl_6, $[Rh(nbd)Cl]_2$, and $Fe(acac)_3$ were used as received. *n*-Bu_4Sn was distilled by the usual manner and used as toluene solution (200 mmol/L). All the reagents in monomer synthesis were used as purchased without further purification. All the monomers were prepared according to the reported method [3c].

Measurements. The molecular weights of the polymers were estimated by gel permeation chromatography ($CHCl_3$ as an eluent, polystyrene standards). IR spectra, UV-visible spectra, and NMR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, and a JEOL GSX-270 spectrometer, respectively. Thermogravimetric analyses (TGA) were conducted in air on a Perkin-Elmer TGA7 thermal analyzer.

Polymerization. Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. Transition metal catalysts and organometallic cocatalysts were used as purchased. Isolation of the polymer was conducted by precipitation into an excess of methanol, and their yields were determined by gravimetry. Detailed polymerization conditions were as follows unless specified. Mo- and W-catalyzed polymerizations: in toluene, 30°C, 3h, $[M]_0$ = 200 mM, [Cat] = 10 mM, [Cocat] = 20 mM. Rh-catalyzed polymerizations: in toluene, 30°C, 1h, $[M]_0$ = 200 mM, [Cat] = [Cocat] = 2 mM. Fe-catalyzed polymerizations: in toluene, 30°C, 24h, $[M]_0$ = 200 mM, [Cat] = 10 mM, [Cocat] = 30 mM.

Acknowledgment.

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